CHAPTER 4

ABIOTIC PROCESSES AFFECTING THE REMEDIATION OF CHLORINATED SOLVENTS

David M. Cwiertny[1] and Michelle M. Scherer[2]

[1]University of California at Riverside, Riverside, CA 92521; [2]The University of Iowa, Iowa City, IA 52242

4.1 INTRODUCTION

Abiotic processes, such as sorption, volatilization and chemical transformation, play an important role in the natural attenuation and treatment of chlorinated solvents. In this chapter, an overview of the principles governing these processes in the context of chlorinated solvent remediation and treatment is presented. This discussion includes a brief introduction to sorption processes and volatilization, with most attention focused on abiotic transformation pathways because of the recent advances in this area and the increasing interest in applying monitored natural attenuation (MNA) to chlorinated solvent plumes. The chapter is not meant to be a comprehensive review of the literature, but rather highlights basic information on key abiotic processes that may impact remedial technology implementability.

4.2 SORPTION PROCESSES

Both the mobility and bioavailability of chlorinated solvents can be significantly influenced by sorption onto aquifer solids. The term sorption does not imply a particular mechanism of removal, but rather broadly describes the partitioning of a chemical from aqueous solution onto or into a solid phase (Stumm, 1992). Sorption of chlorinated solvents can occur onto mineral phases or organic carbon materials present in the aquifer solids (Pankow et al., 1994). The degree of sorption is controlled mostly by properties of the chlorinated solvent (e.g., solubility and polarity) and the aquifer material (e.g., organic carbon and clay-fraction contents), and to a lesser extent by the geochemical conditions of the aquifer (i.e., pH, temperature, ionic strength, and other dissolved chemicals). As a result of sorption processes, chlorinated solvents often move more slowly than groundwater, a process referred to as retardation (Fetter, 1999).

4.2.1 A*b*sorption versus A*d*sorption

For chlorinated solvents (as for most hydrophobic organic compounds) there are thought to be two primary mechanisms of sorption: absorption and adsorption (Stumm, 1992). As discussed in Chapter 2, chlorinated solvents are moderately hydrophobic with $\log K_{\mathrm{ow}}$ values ranging from about 1 to 3. The hydrophobic nature (i.e., tendency to not be in water) of most organic contaminants results in a physical partitioning out of water into sediment organic

H.F. Stroo and C.H. Ward (eds.), *In Situ Remediation of Chlorinated Solvent Plumes*,
doi: 10.1007/978-1-4419-1401-9_4,

matter via absorptive partitioning that is three-dimensional in nature. Sorption onto minerals or other solid materials present in aquifer solids, on the other hand, occurs via an electrostatic or chemical surface adsorption reaction that is considered more of a two-dimensional process (Weber and DiGiano, 1996).

Absorptive partitioning has historically been considered the dominant mechanism for sorption of hydrophobic organic compounds in aquifers containing a significant fraction of organic carbon (fraction of organic carbon, $f_{oc} > 0.001$) (Schwarzenbach and Westall, 1981; Chiou et al., 1983). Surface adsorption to minerals was considered to be significant only in low carbon, high clay aquifers (Karickhoff, 1984). Direct evidence for sorption of organic compounds onto minerals (Perlinger et al., 1993; Mader et al., 1997), however, coupled with studies that were observing more sorption than expected based on absorptive partitioning, led to more recognition of the importance of surface adsorption processes (Mackay et al., 1986a).

In addition to adsorption onto minerals, the role of different types of organic matter has also become more evident. Organic matter in sediments can range from fresh materials containing low carbon and high hydrogen and oxygen contents (i.e., the so-called *soft* carbon, such as peat), or more processed material with high carbon and low hydrogen and oxygen contents (i.e., the so-called *hard* carbon, such as coal and kerogen). Adsorption to the more polymerized soil carbon is now recognized to be a significant sorption mechanism for many organic compounds, including chlorinated solvents (Grathwohl, 1990; Ball and Roberts, 1991; Weber et al., 1992; Jeong and Werth, 2005). The increasing evidence for adsorption to both minerals and polymerized organic carbon has led to a more complete view of sorption including the following mechanisms: (1) absorptive partitioning into *soft* C, (2) adsorption to polymerized *hard* C and (3) adsorption to minerals.

Several research groups have been actively engaged in developing models that incorporate both absorption and adsorption processes to describe chlorinated solvent sorption. For an insightful discussion and synthesis of the literature in this area the reader is referred to a recent review by Allen-King et al. (2002).

4.2.2 Measuring and Estimating Sorption

4.2.2.1 Sorption Isotherms

Sorption of chlorinated solvents is often estimated from batch and column experiments conducted in the laboratory, although a variety of field methods also have been developed (Pankow and Cherry, 1996). In laboratory batch experiments, sorption of trichloroethene (TCE) can be estimated by exposing aquifer solids to dissolved TCE, and measuring the initial and final concentration of TCE in the water after sufficient time for equilibration (C_o and C_W, milligrams per liter [mg/L]). It is important to note that kinetics of sorption can be slow and it can be difficult to conduct the long-term experiments required for equilibration to occur (Pignatello and Xing, 1996; Heyse et al., 2002).

The amount of TCE sorbed is then determined by subtracting the final concentration from the initial concentration based on the mass balance equation for TCE given below. C_S is the amount sorbed, typically in mass of TCE per mass of aquifer solid (milligrams per kilogram [mg/kg]), M is the mass of the solid (kg), and V is the volume of water (L). This assumes that the volume does not change significantly during the sorption experiment. If the final concentration of TCE is measured before reaching equilibrium, the equilibrium partitioning of TCE onto the aquifer material will be underestimated.

$$C_oV = C_WV + C_SM \tag{Eq. 4.1}$$

$$C_S = (C_oV - C_WV)/M \tag{Eq. 4.2}$$

These measurements can be done over a range of dissolved TCE concentrations, and a plot of C_S versus C_W is referred to as a sorption isotherm ("isotherm" indicates that the sorption measurements are collected at a constant temperature).

Figure 4.1 shows two of the more common isotherm models used to describe sorption of chlorinated solvents: linear and Freundlich. Both are equilibrium models, and assume the kinetics of sorption are fast relative to the time scale of the experiment. The linear model is convenient in that a single partition coefficient, K_d (L/kg), derived from the slope of the isotherm, can be used to estimate the amount of sorption. Sorption that is concentration-dependent (i.e., nonlinear sorption), however, has been observed by numerous researcher groups (Allen-King et al., 1996; Xing and Pignatello, 1997; Chiou and Kile, 1998). The nonlinearity is typically described using a Freundlich isotherm with $n < 1$ which captures the decreasing sorption with increasing concentration. At low chlorinated solvent concentrations, however, the Freundlich is approximately linear, and a K_d can be estimated from the linear segment.

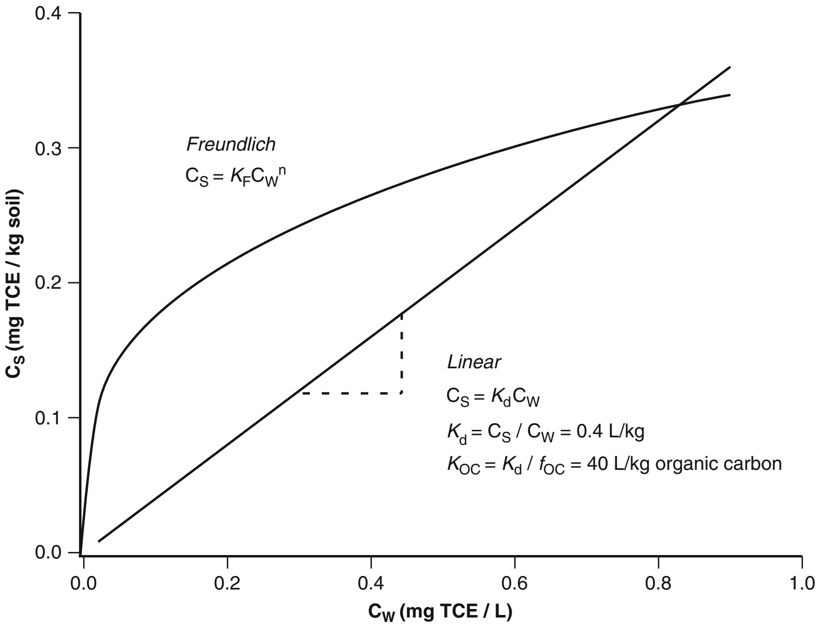


Figure 4.1. Illustration of a linear and nonlinear (Freundlich) sorption isotherm and the corresponding equations. An f_{OC} of 0.01 was used to estimate K_{OC}. The third common isotherm, a Langmuir isotherm, is not shown because a Langmuir pattern with surface site saturation is not typically observed for sorption of chlorinated solvents.

4.2.2.2 K_{ow}-K_{oc}-f_{oc} Paradigm

K_d values measured from a variety of solids and organic compounds have been shown to increase linearly with higher fractions of organic carbon in the solid phase (i.e., $K_d \; \alpha \; f_{OC}$)

(Schwarzenbach and Westall, 1981; Karickhoff, 1984). These observations have led to the common practice of estimating an organic carbon/water partitioning coefficient K_{OC} (L/kg-carbon) by dividing the K_d by f_{OC}.

$$K_{OC} = K_d / f_{OC} \tag{Eq. 4.3}$$

Measured K_d values, however, are often not available and methods for estimating K_{OC} values based on properties of the organic compound and aquifer material have been developed. Two properties of the organic compound commonly used to estimate K_{OC} values are K_{OW} and solubility. Solubility (S) tends to be a good predictor of partitioning between organic carbon and water because the less soluble the compound, the more hydrophobic the compound tends to be and the greater its tendency to partition out of water.

The most widely used method for estimating K_{OC} is based on one parameter linear free energy relationships (op-LFERs) developed from correlations between logK_{OC} and logK_{OW} that take the form of Equation 4.4 (e.g., Schwarzenbach and Westall, 1981; Karickhoff, 1984):

$$\log K_{OC} = a \log K_{OW} + b \tag{Eq. 4.4}$$

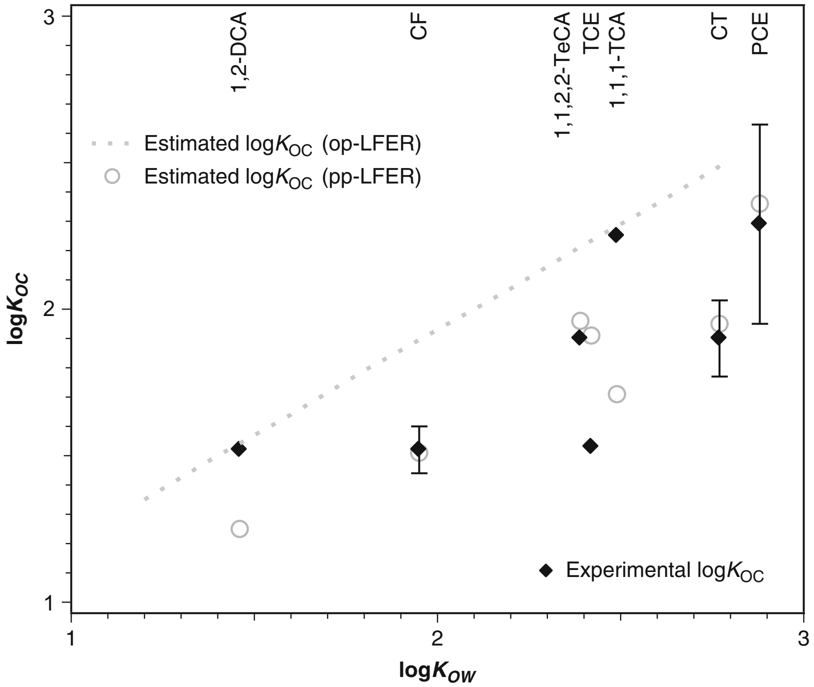


Figure 4.2. Experimental and estimated values of log organic carbon/water partitioning coefficients (logK_{OC}) versus logK_{OW} values for selected chlorinated solvents. Diamond markers represent experimental values of logK_{OC} as summarized in Nguyen et al. (2005) plotted versus logK_{OW} values listed in Table 2.2. Estimated values are based on two example estimation methods reported in the literature. The most common method is a one-parameter LFER based on logK_{OW} values shown as a dashed line. The widely used one-parameter LFER (op-LFER) developed by Schwarzenbach and Westall in 1981 (logK_{OC} = 0.72 logK_{OW} + 0.49) is shown as a dashed line (Schwarzenbach and Westall, 1981). A more recent method based on polyparameter LFERs (pp-LFER) is shown in circles (Nguyen et al., 2005).

There are numerous types of these correlations available for many different sets of organic compounds and the reader is again referred to the review by Allen-King et al. for a compilation of correlations and *a* and *b* parameters (Allen-King et al., 2002, Table 3). The practice of predicting sorption behavior based on K_{OW} values and f_{OC} measurement has become so entrenched that it is often referred to as the "K_{OW}–K_{OC}–f_{OC} paradigm". An example calculation to estimate the K_d value for TCE is shown below using the LFER developed by Schwarzenbach and Westall (1981). Predicted K_d values for several other chlorinated solvents are shown as a dashed line in Figure 4.2.

As more studies have been done and more field data have been collected, it has become clear that this approach has some limitations, particularly when applied to compounds that tend to sorb via more adsorptive or site-specific interactions (Karickhoff, 1984; Allen-King et al., 1996; Chiou and Kile, 1998). For example, Figure 4.2 shows marked deviation from linearity for a plot of experimentally determined $\log K_{OC}$ values versus $\log K_{OW}$ values for nine chlorinated solvents taken from a recent critical review by Nguyen et al. (2005). For more non-polar chemicals, such as many polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), less deviation from linearity was observed in plots of $\log K_{OC}$ versus $\log K_{OW}$ suggesting that one-parameter LFERs are a reasonable approach for estimating K_{OC} values for these compounds (Nguyen et al., 2005).

Example 1: K_{OW}–K_{OC}–f_{OC} Paradigm
Estimating K_d for TCE

1. Measure or look up $\log K_{OW}$ for TCE.

   $\log K_{ow} = 2.53$ (Mackay et al., 1993)

2. Estimate K_{OC} for TCE from a correlation with K_{OW}.

   $\log K_{OC} = a \log K_{OW} + b$

   $a = 0.72 \quad b = 0.49$ (Schwarzenbach and Westall, 1981)

   TCE $\log K_{OC} = 2.31$

3. Measure or estimate organic carbon.

   $f_{OC} = 0.01$ (1% organic carbon (OC) content)

4. Calculate a K_d for TCE from $K_d = K_{OC}\, f_{OC}$

   $K_d = (10^{2.31}$ L/kg OC)(0.01 kg OC/kg solids) = **2.04 L/kg solids**

5. Incorporate K_d into transport equation such as advection dispersion equation (ADE) to predict contaminant retardation. For example, a linear retardation factor, which is the ratio of average linear velocity of the groundwater to that of TCE, can be estimated from:

   $\nu/\nu_{TCE} = R = 1 + \rho_b K_d / \theta_W$ (Pankow and Cherry, 1996)

   ρ_b = soil bulk density and θ_W = water-filled porosity

   $R = 1 + (1.81 \text{ kg/L})(2.04 \text{ L/kg}) / 0.33 = \mathbf{12.1}$

   This implies that TCE will migrate in such an aquifer about **12** times slower than the groundwater. Note, however, there are some important simplifying assumptions in this estimate: (1) equilibrium, that is, rapid sorption kinetics compared to groundwater flow and reversible sorption; and (2) linear sorption, that is, C_S versus C_W is linear and therefore independent of concentration.

To address some of the limitations of the K_{OW}–K_{OC}–f_{OC} paradigm, polyparameter LFERs (pp-LFERs) have been developed that take into account multiple molecular interactions between organic compounds and water. For comparison, the $\log K_{OC}$ values predicted from a pp-LFER are also included in Figure 4.2. The pp-LFER predicts K_{OC} values that are closer to the experimental values for three compounds whose K_{OC} values were determined from multiple experimental measurements—chloroform, carbon tetrachloride and perchloroethene (CF, CT, and PCE, respectively). These results suggest that the pp-LFER may provide a more robust method than the traditional $\log K_{OC}$–$\log K_{OW}$ relationships typically used for estimating $\log K_{OC}$ values for chlorinated solvents (Nguyen et al., 2005).

Another important limitation of the K_d–f_{OC} calculations illustrated in Figure 4.1 is that the K_d estimates are often much lower than those observed in the field. The greatest deviations appear to be associated with aquifers containing hard carbon materials, such as kerogen or coal, or in aquifers with low concentrations of contamination (Allen-King et al., 2002).

4.2.2.3 Effect of Sorption on Chlorinated Solvent Transport

The influence of sorption on the mobility of chlorinated solvents has been demonstrated numerous times, with perhaps the most famous demonstration being the Stanford-Waterloo experiment (Mackay et al., 1986b). As part of this experiment, PCE, CT and hexachloroethane (HCA) were injected into an unconfined sandy aquifer near the Canadian Forces Base Borden. Chlorinated solvent concentrations were monitored over time and compared to chloride and bromide tracers.

As expected, the PCE and CT plumes were retarded with respect to chloride and bromide. Also, as anticipated, PCE, which is more hydrophobic than CT, moved slower (Roberts et al., 1986). The average retardation factor observed in the Stanford-Waterloo experiment was 4.5 (Roberts et al., 1986), which is relatively low and consistent with the relatively low K_{OW} of these compounds. Retardation factors reported for chlorinated solvents are generally low, often below 10 (Pankow and Cherry, 1996). The measured retardation factors are higher than the values predicted using the K_{OW}–K_{OC}–f_{OC} paradigm outlined above, but are within a factor of two to five.

The plumes also displayed some unexpected behavior, including an increase in retardation factors over time and longer plume lengths than the chloride and bromide plumes (at the same distance). Over the last two decades, an extensive amount of research has focused on understanding and explaining the transport of PCE and CT in this aquifer, and the reader is referred to Allen-King et al. (2006) for recent insights on these plumes.

4.3 VOLATILIZATION PROCESSES

Volatilization is the process by which a chlorinated solvent is transferred into air from either water or a solid phase (Thomas, 1982b). This process influences the fate of chlorinated solvents because solvent vapors can exhibit different reactivities and rates of transport than species dissolved in water or sorbed to aquifer solids. Although chlorinated solvents are generally considered relatively volatile, several variables influence their mass transfer between water and air or solids and air. For example, chemical factors that impact the rate of chlorinated solvent partitioning between water and air include a compound's aqueous solubility (S), its vapor pressure ($p°$), its molecular diffusivities in air (D_a) and water (D_w), and its equilibrium air-water partitioning coefficient ($K_{\text{air-water}}$) (Thomas, 1982a). Environmental factors such as wind-speed and the degree of mixing in air and water will also contribute.

The following discussion of volatilization begins by examining the simple case of air-water partitioning at equilibrium, where the chlorinated solvent distribution between phases can be predicted using either Raoult's Law or Henry's Law. Next, the role that volatilization plays in subsurface contamination by chlorinated solvents, particularly the transport of chlorinated solvent vapor in the vadose zone, is discussed. Models for estimating the rate of chlorinated solvent volatilization will not be discussed, but the references by Thomas (1982a, 1982b) and

Schwarzenbach et al. (2003) provide detailed presentations of this topic. Treatment strategies (such as air sparging) that take advantage of the high volatility of chlorinated solvents for subsurface remediation are covered elsewhere in this monograph.

4.3.1 Air-Water Partitioning at Equilibrium

As discussed in Chapter 2 (see Figure 2.3), chlorinated solvents will partition between water, air and solids. The focus of this section is their partitioning between water and air in a two-phase system at equilibrium. For air in contact with an aqueous solution of chlorinated solvent, equilibrium is defined as the state in which there is no net rate of solvent transfer between air and water. Of primary interest is the concentration of the chlorinated solvent in air (expressed as a partial pressure with units such as atmospheres [atm]) relative to its concentration in water once equilibrium is established. For this scenario, two possible relationships can be used to describe air-water partitioning. As will be discussed, determining which relationship is most appropriate will depend upon the amount of the chlorinated solvent dissolved in water.

The first approach for describing air-water partitioning is Raoult's Law (Equation 4.5) which states that the equilibrium partial pressure of a chlorinated solvent (p_{RX}) is equal to the product of the mole fraction of the chlorinated solvent in the aqueous mixture (X_{RX}) and the vapor pressure of the chlorinated solvent ($p_{\mathrm{RX}}{}^{\mathrm{o}}$).

$$p_{\mathrm{RX}} = X_{\mathrm{RX}} \cdot p_{\mathrm{RX}}{}^{\mathrm{o}} \tag{Eq. 4.5}$$

In Equation 4.5, X_{RX} represents a measure of the aqueous-phase concentration of a chlorinated solvent. Values of X_{RX} are dimensionless and are defined as the number of moles of dissolved chlorinated solvent divided by the total number of moles present in the aqueous mixture. Values of $p_{\mathrm{RX}}{}^{\mathrm{o}}$, which represent the saturation concentration of a chlorinated solvent in air, are provided in Table 2.2. Thus, for air in contact with an aqueous chlorinated solvent mixture, the equilibrium gas-phase concentration of the solvent is proportional to its concentration in water, and the constant of proportionality for this relationship is the solvent's vapor pressure.

There are limitations to the application of Raoult's Law. Typically, it is only applied when the concentration of the chlorinated solvent in the aqueous mixture is very high (e.g., when X_{RX} approaches 1) or for non-aqueous mixtures in which all chemical components of the mixture possess similar chemical structures (e.g., a mixture of several chlorinated solvents) (Sawyer et al., 1994). When the dissolved chlorinated solvent is present at low concentration Raoult's Law fails, and an alternative approach is required.

In the case of dilute chlorinated solvent solutions, Henry's Law is used to describe equilibrium air-water partitioning. Similar to Raoult's Law, Henry's Law (Equation 4.6) also states that the equilibrium chlorinated solvent partial pressure above an aqueous solvent mixture is proportional to the chlorinated solvent's dissolved concentration.

$$p_{\mathrm{RX}} = K_{\mathrm{H}}{}' \cdot X_{\mathrm{RX}} \tag{Eq. 4.6}$$

Whereas the constant of proportionality in Raoult's Law is the vapor pressure of the chlorinated solvent, Henry's Law uses an alternative proportionality constant, $K_{\mathrm{H}}{}'$, referred to as the Henry's Law constant. The use of $K_{\mathrm{H}}{}'$ rather than $p_{\mathrm{RX}}{}^{\mathrm{o}}$ accounts for unfavorable energetic interactions that occur between the chlorinated solvent and water in relatively dilute solutions.

An important consideration in the application of Henry's Law is the units associated with the chlorinated solvent concentrations in air and water. In Equation 4.6, $K_{\mathrm{H}}{}'$ is expressed in units of pressure, as mole fractions are dimensionless. More commonly, however, Henry's Law constants are reported with the aqueous concentration of the chlorinated solvent ($C_{\mathrm{RX}}(\mathrm{H_2O})$) expressed on a molar basis (e.g., moles of RX per L of H_2O), as shown in Equation 4.7.

$$K_{\mathrm{H}}' = \frac{p_{\mathrm{RX}}}{C_{\mathrm{RX}}(\mathrm{H_2O})}\left(\text{units of } \frac{atm \cdot m^3}{mol}\right) \qquad \text{(Eq. 4.7)}$$

Another frequently used alternative is the dimensionless Henry's Law constant ($K_{\mathrm{H}}{}^{*}$ in Equation 4.8) in which the concentrations of the chlorinated solvent in water and air *both* are expressed on a molar basis (e.g., moles of RX per L of water and moles of RX per L of air, respectively).

$$K_{\mathrm{H}}^{*} = \frac{C_{\mathrm{RX}}(\mathrm{air})}{C_{\mathrm{RX}}(\mathrm{H_2O})}\ \text{(dimensionless)} \qquad \text{(Eq. 4.8)}$$

The dimensionless Henry's Law constant is important because it can be used to develop expressions for the relative amounts of a chlorinated solvent in a closed air-water system that are entirely dependent upon known system parameters (e.g., the volumes of air and water) and the value of $K_{\mathrm{H}}{}^{*}$ (see text box for a sample calculation).

For chlorinated solvents, values of the Henry's Law constant can be reasonably approximated from the ratio of the chlorinated solvent vapor pressure ($p_{\mathrm{RX}}{}^{\mathrm{o}}$) to the aqueous solubility of the chlorinated solvent (S) (Schwarzenbach et al., 2003). These data are provided for chlorinated solvents in Table 2.2 of Chapter 2. Furthermore, a plot of $p_{\mathrm{RX}}{}^{\mathrm{o}}$ as a function of S using these data is shown in Figure 4.3, in which the diagonal dashed lines represent values of the Henry's Law constant. Note that as a result of the units associated with values of $p_{\mathrm{RX}}{}^{\mathrm{o}}$ and S in Table 2.2 in Chapter 2, the Henry's Law constants in Figure 4.3 have units of atmosphere·cubic meter per mole (atm·m^3/mol). Figure 4.3 illustrates that while both $p_{\mathrm{RX}}{}^{\mathrm{o}}$ and S generally increase

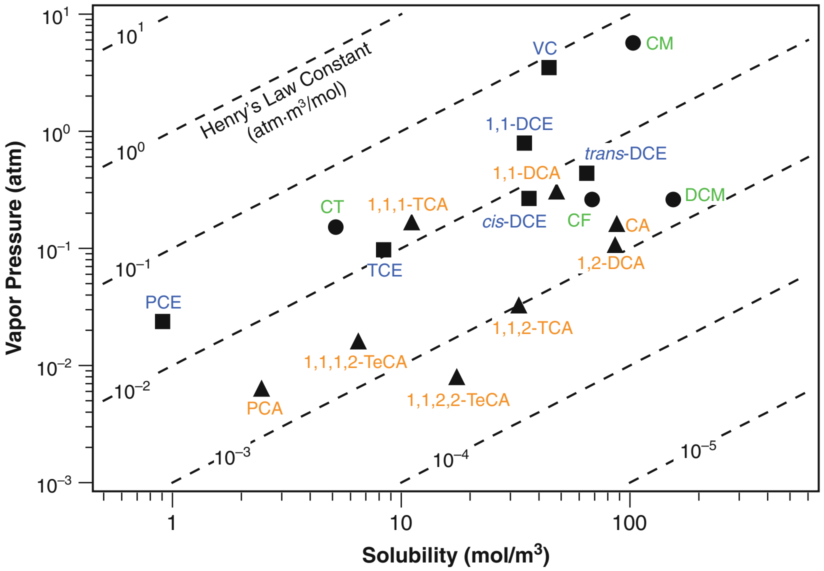


Figure 4.3. Plot of chlorinated solvent vapor pressures as a function of chlorinated solvent solubilities. Values for vapor pressure and solubility are provided in Table 2.2. Dashed lines indicate values of the Henry's Law constant (K_H with units of atm·m^3/mol). Data for chlorinated methanes are shown as circles, chlorinated ethanes as triangles, and chlorinated ethenes as squares. Adapted from Thomas, 1982a.

as the number of chlorine substituents on a solvent decreases, comparable trends in Henry's Law constants are not observed.

Several chemical and environmental variables can influence equilibrium partitioning of a chlorinated solvent in an air-water system. With respect to groundwater contamination, three variables of importance are temperature, the presence of organic co-contaminants and the concentration of dissolved ions (e.g., Na^+, Ca^{2+}, Cl^-, SO_4^{2-} and HCO_3^-). Generally, chlorinated solvent air-water partitioning increases with temperature and ionic strength, whereas the presence of appreciable concentrations of organic co-contaminants (such as other chlorinated solvents) will cause the extent of equilibrium air-water partitioning to decrease (Schwarzenbach et al., 2003).

4.3.2 Vapor Phase Transport of Chlorinated Solvents in the Vadose Zone

While air-water partitioning is likely to be unimportant in saturated groundwater systems, it represents an important process for pollutant source zones present in unsaturated environments such as the vadose zone (Brusseau, 1994). In the unsaturated zone, chlorinated solvent vapors can exist in the air-filled pore space, and the behavior, fate and environmental consequences of such gas phase species must be considered. For example, the downward migration of solvent vapors present in the unsaturated zone can represent an important source of pollution for the underlying groundwater in the saturated zone (Schwille, 1984; Schwille, 1988; Conant et al., 1996).

Unlike dissolved species in aqueous solution, transport of chlorinated solvent vapors is believed to be governed by molecular diffusion (Conant et al., 1996; Jellali et al., 2003), although advection resulting from density gradients may also be important (Mendoza and Frind, 1990a; Mendoza and Frind, 1990b). As molecular diffusivities for chlorinated solvents in air are large relative to water ($D_{air} \sim 10^{-2}$ square centimeters per second (cm^2/s) whereas $D_{water} \sim 10^{-5}$ cm^2/s) (Schwarzenbach et al., 2003), a diffusion dominated transport mechanism allows for the rapid proliferation of a vapor phase contaminant plume, resulting in a much larger area of subsurface contamination than might be anticipated if vapor migration in the vadose zone were ignored (Brusseau, 1994). Aquifer characteristics such as organic matter content (Conant et al., 1996) and water vapor content (e.g., Batterman et al., 1995) will play critical roles in gas phase transport, with partitioning into aqueous phases and organic phases retarding the rate of chlorinated solvent vapor migration.

Example 2: Air-Water-Solid Partitioning
Chlorinated Solvent Mass Balance in a Contaminated Subsurface

Q: Consider a waste site where a total of 150 kg of carbon tetrachloride (CT) has been accidentally discharged into an underground aquifer. The CT plume impacts a total volume in the subsurface of 1×10^6 L, and the impacted aquifer material has an organic carbon content of 1% and a bulk density of 2.0 kg/L. The aquifer solids have a porosity of 0.30 and 50% of the pore space is filled with water, whereas the other 50% is air. From Mackay et al. (1993), CT has a Henry's Law constant of 28.9×10^{-3} atm·m^3/mol at 25 degrees Celsius (°C). From Nguyen et al. (2005), the K_{OC} for chloroform is $10^{1.9}$ L/kg of OC. Assume equilibrium exists everywhere at the site and determine the fraction of CT in the air space, in the water, and sorbed to the aquifer material. How does the partitioning of CT change if the aquifer material has an organic carbon content of 3%? Repeat these calculations for 1,1,2,2-TeCA, which has the same K_{OC} value as CT, but a much smaller Henry's Law constant (0.44×10^{-3} atm·m^3/mol).

A: We start by developing an expression for the total mass of CT in our system, accounting for its presence in water, in air, and sorbed on aquifer solids.

$$Total\ Mass = Mass_{water} + Mass_{air} + Mass_{solid} \tag{i}$$

$$Total\ Mass = C_{water}V_{water} + C_{air}V_{air} + C_{solid}M_{solid} \tag{ii}$$

In (ii) C_{water} has units of mass of CT per L water and C_{air} has units of mass of CT per L air. C_{solid}, on the other hand, uses a different convention with units of mass of CT per kg solid. M_{solid} is the mass of solids present in the aquifer with units of kg.

The fraction of CT in water (f_{water}) is obtained by dividing the mass of CT in water ($C_{water}V_{water}$) by the total CT mass in our system.

$$f_{water} = \frac{C_{water}V_{water}}{C_{water}V_{water} + C_{air}V_{air} + C_{solid}M_{solid}} \tag{iii}$$

At equilibrium, CT air-water partitioning is described by Henry's Law; water-solid partitioning is determined from the K_d value for CT.

$$K_H^* = \frac{C_{air}}{C_{water}} \tag{iv}$$

$$K_d = K_{OC} \times f_{OC} = \frac{C_{solid}}{C_{water}} \tag{v}$$

By incorporating (iv) and (v) into our expression for f_{water} (iii), we obtain:

$$f_{water} = \frac{C_{water}V_{water}}{C_{water}V_{water} + K_H^* C_{water}V_{air} + K_{OC}f_{OC}\,C_{water}\,M_{solid}} \tag{vi}$$

which simplifies to the following expression dependent entirely upon known system parameters.

$$f_{water} = \frac{1}{1 + K_H^* \frac{V_{air}}{V_{water}} + K_{OC}f_{OC}\,\frac{M_{solid}}{V_{water}}} \tag{vii}$$

The fraction of CT in water can now be determined from the known characteristics of the aquifer material.

V_{water} can be calculated from the total site volume (1×10^6 L), the site porosity (0.3) and the percentage of pore space comprised of air (0.5).

$$V_{water} = (1 \times 10^6 \mathrm{L})(0.3)(0.5) = 1.5 \times 10^5 \mathrm{L}$$

V_{air} can be calculated in a similar fashion

$$V_{air} = (1 \times 10^6 \mathrm{L})(0.3)(0.5) = 1.5 \times 10^5 \mathrm{L}$$

The solid to water ratio (M_{solid} / V_{water}) can then be determined from the bulk density of the aquifer material and V_{water}.

$$\frac{M_{solid}}{V_{water}} = \frac{(2.0\ kg/L)(1 \times 10^6 L)}{1.5 \times 10^5 L} = 13.3\ kg/L$$

Before solving for f_{water}, note that our expressions use the dimensionless Henry's Law constant (K_H^*), although we are provided with values of K_H. Conversion between K_H and K_H^* can be accomplished using PV = nRT, where R = 8.205×10^{-5} m^3/mol·K and T is absolute temperature in Kelvin.

$$K_H^*(dimensionless) = \frac{K_H\left(\frac{m^3 \cdot atm}{mol}\right)}{R\ T} = 1.18 \tag{viii}$$

The fraction of CT in water can now be determined from (vii):

$$f_{water} = 0.078$$

and the corresponding mass and concentration of CT in water are calculated as follows:

$$M_{water} = (f_{water})(Total\ Mass) = 11.8\ \text{kg}$$

$$C_{water} = M_{water}/V_{water} = 79\ \text{mg/L} = 79\ \text{ppm}$$

We can now solve for the concentration in air using Henry's Law.

$$C_{air} = (K_H^*)(C_{water}) = 93\ \text{mg/L}$$

This, in turn, allows the total mass of CT in air, and the fraction of CT in air to be calculated.

$$M_{air} = (C_{air})(V_{air}) = 14\ \text{kg}$$

$$f_{air} = M_{air}/(Total\ mass) = 0.093$$

Finally, by mass balance, the results obtained for the amount of CT in air and water can be used to determine the amount of CT sorbed to the aquifer solids.

$$f_{solid} = 1 - f_{water} - f_{air} = 0.83$$

$$M_{solid} = Total\ Mass - M_{air} - M_{water} = 124\ \text{kg}$$

$$C_{solid} = 62\ \text{mg of CT per kg solid}$$

About 83% of the CT is sorbed onto the solids with about 9% in air and 8% in water.

We can now repeat the calculations for f_{OC} = 3% and for 1,1,2,2-TeCA. These results, as well as those derived above, are summarized in the following table.

	CT $f_{OC} = 1\%$	**CT** $f_{OC} = 3\%$	**1,1,2,2-TeCA** $f_{OC} = 1\%$	**1,1,2,2-TeCA** $f_{OC} = 3\%$
f_{solid}	0.83	0.94	0.91	0.97
f_{water}	0.08	0.03	0.09	0.03
f_{air}	0.09	0.03	0.001	0.0006
C_{solid} (mg/kg)	62	70	68	73
C_{water} (mg/L)	79	30	86	31
C_{air} (mg/L)	93	35	2	0.5
M_{solid} (kg)	124	140	137	145
M_{water} (kg)	12	5	13	5
M_{air} (kg)	14	5	0.2	0.08

In all instances, sorption into organic matter in the aquifer material is the dominant partitioning process for both CT and 1,1,2,2–TeCA. As expected, the amount of sorbed chlorinated solvent increases with f_{oc}, whereas the contribution of gas phase partitioning is greatest with increasing Henry's Law constant. Consideration of sorption and gas phase partitioning is important in the context of the abiotic reaction pathways discussed in the subsequent portions of this chapter, as the reactivity of the chlorinated solvent will be influenced by its form in the environment.

4.4 ABIOTIC TRANSFORMATION PROCESSES

This section presents a review of the prominent abiotic transformation pathways for chlorinated solvents. The focus is on natural environments, but where relevant, some engineering technologies will also be discussed. While these transformation pathways may reduce the persistence of chlorinated solvents in subsurface environments, they can also yield product species that exhibit considerably different behavior in groundwater. It is therefore important to understand the factors that influence the distribution of transformation products, as well as the rates of chlorinated solvent transformation.

Abiotic transformation reactions of chlorinated solvents can be divided into two broad categories. The first are those reactions in which the average oxidation state of carbon in the chlorinated solvent does not change as a result of reaction. Common examples of transformation pathways from this class include substitution and non-reductive elimination (or simply, elimination) reactions. The other broad class of reactions is that in which the average carbon oxidation state changes during reaction due to a net transfer of electrons between reactants. Reactions involving electron transfer are known as reduction and oxidation (or redox) reactions. Environmentally relevant examples of reactions from each class are given in Table 4.1 and discussed in more detail below.

Table 4.1. Common Classes of Abiotic Transformation Pathways of Chlorinated Solvents and Environmentally Relevant Examples

Reaction	Relevant Examples
1—No change in average carbon oxidation state	
Nucleophilic Substitution (predominantly S_N2)	
$R\text{-}X + Nuc^- \rightarrow R\text{-}Nuc + X^-$	*Hydrolysis:* $CH_3Cl + H_2O \Rightarrow CH_3\text{-}OH + H^+ + Cl^-$ (chloromethane ⇒ methanol) $CH_2Cl\text{-}CH_3 + OH^- \Rightarrow CH_3\text{-}CH_2OH + Cl^-$ (chloroethane ⇒ ethanol) *Thiol substitution:* $CH_2Br\text{-}CH_2Br + 2HS^- \Rightarrow CH_2SH\text{-}CH_2SH + 2Br^-$ (1,2-dibromoethane ⇒ 1,2-ethanedithiol)
Non-reductive Elimination (predominantly E_2)	
$R_1X\text{-}R_2H + B^- \rightarrow R_1{=}R_2 + BH + X^-$	*Dehydrohalogenation:* $Cl_2HC\text{-}CCl_3 + H_2O \Rightarrow Cl_2C{=}CCl_2 + H_3O^+ + Cl^-$ (PCA ⇒ PCE) $Cl_2HC\text{-}CHCl_2 + OH^- \Rightarrow Cl_2C{=}CHCl + H_2O + Cl^-$ (1,1,2,2-TeCA ⇒ TCE)
2—Change in carbon oxidation state[a]	
Reduction	
Hydrogenolysis $RX + 2e^- + H^+ \rightarrow RH + X^-$	$CHCl_3 + 2e^- + H^+ \Rightarrow CH_2Cl_2 + Cl^-$ (chloroform ⇒ dichloromethane) $CH_3\text{-}CCl_3 + 2e^- + H^+ \Rightarrow CH_3\text{-}CHCl_2 + Cl^-$ (1,1,1-TCA ⇒ 1,1-DCA) $CH_2{=}CCl_2 + 2e^- + H^+ \Rightarrow CH_2{=}CHCl + Cl^-$ (1,1-DCE ⇒ vinyl chloride)
Reductive β-elimination $R_1X\text{-}R_2X + 2e^- \rightarrow R_1{=}R_2 + 2X^-$	$CCl_3\text{-}CCl_3 + 2e^- \Rightarrow CCl_2{=}CCl_2 + 2Cl^-$ (HCA ⇒ PCE) $CHCl{=}CCl_2 + 2e^- \Rightarrow HC{\equiv}\, CCl + 2Cl^-$ (TCE ⇒ chloroacetylene)
Reductive α-elimination $R_1\text{-}R_2X_2 + 2e^- \rightarrow R1\text{-}\ddot{R}_2 + 2X^-$	$CCl_4 + 2e^- \Rightarrow \ddot{C}Cl_2 + 2Cl^-$ (carbon tetrachloride ⇒ dichlorocarbene) $CH_3\text{-}CHCl_2 + 2e^- \Rightarrow CH_3 - \ddot{C}H + 2Cl^-$ (1,1-DCA ⇒ methyl carbene)

[a] For a discussion of relevant oxidation reactions, please see Chapter 15 in this Volume

4.4.1 Substitution and Elimination Reactions

In the most general terms, substitution and elimination reactions transform chlorinated solvents into new compounds with different chemical structures and less chlorine substituents. Although substitution and elimination reactions are fundamentally different processes, an important shared characteristic is that the average oxidation state of carbon is unchanged by both processes. Thus, although the carbon atoms in chlorinated solvents can exist in many different oxidation states (ranging from –II to +IV), the oxidation state of the chlorinated solvent will always equal that of the reaction product generated via a substitution or elimination transformation pathway.

4.4.1.1 Substitution Reactions

As shown in Table 4.1, substitution reactions involve the addition of a new atom (or group of atoms) to a carbon center of a chlorinated solvent. As a carbon center can be bonded to at most four atoms (called substituents), this addition occurs at the expense of one of the chlorines originally bonded to the reactive carbon. Consequently, the new atom is substituted for chlorine in the reaction product, hence the name "substitution reactions."

For chlorinated solvents, the most environmentally relevant substitution reaction involves the reaction with water. An example is shown in Equation 4.9 for chloromethane (CH_3Cl), which reacts with water to produce methanol.

$$CH_3Cl + H_2O \rightarrow CH_3OH + H^+ + Cl^- \qquad \text{(Eq. 4.9)}$$

This type of reaction, in which a carbon-chlorine bond is broken via reaction with a water molecule (or, as will be discussed later, a hydroxide ion) is commonly referred to as hydrolysis (literally meaning "broken with water"). As in Equation 4.9, the typical products of hydrolysis reactions are alcohols, which can be considered a lesser environmental hazard than chlorinated solvents.

The hydrolysis of chloromethane occurs when the electrons associated with the oxygen in the water molecule are attracted to (or attack) the methyl carbon center, which can be considered slightly electron-deficient because of the electron-withdrawing chlorine substituent. Accordingly, water is called a nucleophile (its electrons make it "nucleus loving"), the carbon center is referred to as an electrophile (its electron deficiency makes it "electron loving"), and the chlorine substituent that is displaced as a result of this reaction is known as the leaving group. As both water and chloromethane are involved in the rate-determining reaction step that simultaneously breaks (e.g., C-Cl) and forms (e.g., C-O) bonds, the overall reaction is bimolecular in nature. Chloromethane hydrolysis is, therefore, classified as an S_N2 reaction, where the abbreviation stands for substitution, nucleophilic, bimolecular.

Although water is not a very reactive nucleophile (Schwarzenbach et al., 2003), it can be considered a key reactant in environmental systems as a result of its high abundance; the concentration of water is ~56 M, whereas the concentration of chlorinated solvents in contaminated groundwater is at most ~10^{-3} M under saturated conditions (see Table 2.2). Hydroxide ions (OH^-) represent another environmentally relevant nucleophile. Hydroxide ion is a more reactive nucleophile than water (Vollhardt and Schore, 1994) that also reacts with chlorinated solvents via an S_N2 mechanism. Additional nucleophiles such as NO_3^-, CN^-, HS^- and SO_3^{2-} are also encountered in natural systems, but their reactions with chlorinated solvents are typically not as significant as reactions with water and hydroxide ions because of their relatively low environmental abundance (Schwarzenbach et al., 2003).

An S_N2 hydrolysis pathway (involving either H_2O or OH^-) is only important for a subset of chlorinated solvents. It is only expected to occur at fully saturated carbon centers (i.e., a carbon atom with single bonds to all substituents), such as those present in chlorinated methanes and ethanes. In contrast, S_N2 hydrolysis is not important for chlorinated ethenes such as TCE, PCE or vinyl chloride (VC). Furthermore, this reaction will only exhibit appreciable rates for mono- and dichlorinated species because steric effects generally limit the successful nucleophilic attack at a fully substituted carbon center such as that present in 1,1,1-trichloroethane (TCA, Cl_3CCH_3). Taking these factors into consideration, product distributions and/or reaction kinetics consistent with an S_N2 hydrolysis mechanism have been observed for chloromethane (Heppolette and Robertson, 1959), dichloromethane (Fells and Moelwyn-Hughes, 1958), CF (Fells and Moelwyn-Hughes, 1959), and 1,2-dichloroethane (1,2-DCA) (Jeffers et al., 1989). Note that the identity of the halide leaving group will considerably influence the tendency for a halogenated solvent to undergo an S_N2 reaction, and the following reactivity trend based upon halide leaving group is well-established (Vollhardt and Schore, 1994): R-F << R-Cl < R-Br < R-I. Mono- and dibrominated methanes and ethanes (e.g., 1,2-dibromoethane), therefore, will react via an S_N2 mechanism at a greater rate than their chlorinated analogues (e.g., 1,2-DCA).

4.4.1.2 Non-Reductive Elimination Reactions

Non-reductive elimination reactions always involve the loss of two substituents (e.g., H and Cl) that are located on neighboring carbon atoms of a chlorinated solvent. Unlike substitution reactions, the loss of these substitutents is not accompanied by the addition of a new atom or group of atoms to the parent molecule. Rather, in order to satisfy the bonding requirements of both carbon centers involved in this reaction, elimination pathways result in an increased bond order (e.g., the formation of a double bond from a single bond) between these adjacent carbon atoms.

As an example, pentachloroethane (PCA) readily undergoes non-reductive elimination to yield PCE (Roberts and Gschwend, 1991):

$$Cl_3CCHCl_2 + OH^- \rightarrow Cl_2C = CCl_2 + H^+ + Cl^- \qquad \text{(Eq. 4.10)}$$

Equation 4.10 is an example of a bimolecular elimination reaction (abbreviated as E_2), in which a base (OH^-) removes a proton from one carbon center while the C-Cl bond on the neighboring carbon simultaneously dissociates in the rate-determining step. While the electrons from the C-Cl bond remain with the chlorine atom after dissociation to produce a free chloride ion, the electrons associated with the proton remain on the carbon, thereby allowing for the increased bond order that is characteristic of elimination reactions. Accordingly, the characteristic product of chlorinated ethane elimination will be an ethene species possessing one less chlorine substituent. Non-reductive elimination reactions that result in the loss of a proton and a halogen atom from a chlorinated solvent are commonly referred to as dehydrohalogenation. More generally, this type of reaction also can be classified as a non-reductive β-elimination because the proton is removed from the β-carbon of the chlorinated solvent (defined as the carbon atom directly adjacent to the center with the most chlorine substituents). Note that water molecules are also capable of reacting with chlorinated solvents via an analogous bimolecular elimination pathway.

In theory, any chemical with hydrogen and chlorine substituents on adjacent carbon centers can react via a dehydrohalogenation pathway. This reaction is most likely to occur, however, when the majority of electron density associated with the hydrogen atom in question has been removed by neighboring substituents that are electron withdrawing (e.g., additional halogen atoms). Under such circumstances, the hydrogen atom can be considered to behave proton-like, and thereby is prone to removal by either a moderate (e.g., H_2O) or strong (e.g., OH^-) base. This is the case for the hydrogen(s) present on PCA (Roberts and Gschwend, 1991) and 1,1,2,2-TeCA (Jeffers et al., 1989), which represent two chlorinated solvents with relatively high rates of dehydrohalogenation at environmentally relevant pH values. Additional species whose reaction kinetics and/or products are consistent with a bimolecular dehydrohalogenation mechanism include 1,1-DCA, 1,1,2-TCA and 1,1,1,2-TeCA, as well as 1,2-DCA at high pH values (Jeffers et al., 1989).

4.4.2 Reduction and Oxidation Reactions

The second broad class of reactions involves the transfer of electrons between chemical reactants. These reactions are referred to as reduction and oxidation (or redox) reactions. For such reactions, one species serves as the electron donor, also known as the reductant, and another species functions as the electron acceptor or the oxidant. During the reaction, the reductant donates electrons and becomes oxidized, while the oxidant accepts electrons and gets reduced. Whether a chlorinated solvent is acting as an electron donor or acceptor can be determined by monitoring changes in the solvent's average carbon oxidation state, values of which are listed in Table 2.2. Reduction of a chlorinated solvent (to a species such as methane or ethane) decreases the average carbon oxidation state of the compound. In contrast, the average carbon oxidation state of a solvent increases as the result of an oxidation reaction (to a species such as carbon dioxide).

The primary focus of this section is the abiotic reduction of chlorinated solvents. Emphasis will be placed on naturally occurring abiotic reduction reactions, but reductive transformations that have been harnessed in field-scale treatment strategies for groundwater remediation will also be introduced. Abiotic oxidation reactions will not be discussed. These reactions, which tend to be less important in the natural environment but are employed in engineered treatment strategies, are discussed in greater detail in Chapter 15.

4.4.2.1 Reductive Transformation Pathways

Generally, the reduction of a chlorinated solvent results in the replacement of a halogen substituent(s) by a hydrogen atom or the formation of a pi-bond (π-bond) system. Reactions of this kind are often therefore broadly referred to as reductive dehalogenation because the solvent loses halogen substituents during the reduction process. A number of reduction pathways exist, however, and the three most relevant to chlorinated solvents (hydrogenolysis, reductive β-elimination, and reductive α-elimination) are discussed below.

The most straightforward reduction pathway is hydrogenolysis, shown below for the reduction of 1,1,1-TCA to 1,1-DCA (Equation 4.11).

$$Cl_3C-CH_3+2e^-+H^+ \rightarrow Cl_2CH-CH_3+Cl^- \qquad \text{(Eq. 4.11)}$$

As shown in Equation 4.11, hydrogenolysis is a net two-electron transfer that replaces a chlorine substitutent with a hydrogen atom. In theory, all classes of chlorinated solvents (methanes, ethanes and ethenes) can be reduced via a hydrogenolysis pathway. Note that for polyhalogenated species such as 1,1,1-TCA, hydrogenolysis will always yield another chlorinated solvent with a lower degree of chlorination.

Another important pathway is reductive β-elimination, shown in Equation 4.12 for the reduction of 1,1,2,2-TeCA to *cis*- or *trans*-1,2-DCE.

$$Cl_2HC-CHCl_2+2e^- \rightarrow CHCl=CHCl+2Cl^- \qquad \text{(Eq. 4.12)}$$

Reductive β-elimination is also a net two-electron transfer process. Unlike hydrogenolysis, this pathway involves the loss of two halogen substituents from adjacent carbon centers (a process commonly referred to as a dihalo-elimination). A characteristic of reductive β-elimination is that the bond order between the two carbon centers increases (i.e., a single bond is transformed to a double bond, or a double bond becomes a triple bond). This pathway will, therefore, transform a polychlorinated ethane into an ethene with a lower degree of halogenation (e.g., HCA to PCE), whereas polychlorinated ethenes will be reduced to acetylene species (which have a carbon-carbon triple bond). As chlorine substituents on adjacent carbon centers (known as vicinal or neighboring halides) are required for this pathway, reductive β-elimination cannot involve polychlorinated methanes.

The last reductive transformation of note is reductive α-elimination, shown in Equation 4.13 for the reduction of 1,1-DCA.

$$Cl_2HC-CH_3+2e^- \rightarrow \ddot{C}H - CH_3+2Cl^- \qquad \text{(Eq. 4.13)}$$

Reductive α-elimination is another two-electron, dihalo-elimination reaction. Unlike reductive β-elimination, however, the two chlorine substituents are lost from the same carbon center (referred to as the α-carbon). Thus, in order for reductive α-elimination to be a viable reduction pathway for a chlorinated solvent, it must possess multiple halogen atoms on the same carbon center, which are sometimes referred to as geminal (meaning “twin”) halides.

A characteristic intermediate in reductive α-elimination is the carbene, which is defined as a neutrally charged carbon center bound to only two substituents and in possession of a lone pair of electrons (Carroll, 1998). Carbenes (such as the methyl carbene in Equation 4.13) are relatively reactive intermediates and consequently will not accumulate in most reductant systems. They participate in a variety of reactions such as coupling and insertion reactions with water molecules (Carroll, 1998) and may therefore allow for reduction products that are quite different from those generated via other reduction pathways.

As a practical consideration, the aforementioned reduction pathways all lead to different product species, and unique pathways may dominate for different combinations of reductants and chlorinated solvents. Moreover, several chlorinated solvents have structural features that may allow them to react by more than one pathway in the presence of a reductant. For instance, *cis*-DCE can react either by hydrogenolysis or reductive β-elimination. Clearly, reductive β-elimination to yield ethene is preferred, as a hydrogenolysis pathway will produce vinyl chloride, which is generally regarded as more toxic.

4.4.2.2 Abiotic Reductants

Abiotic reductants that are commonly found in natural systems include natural organic matter, reduced iron compounds, and reduced sulfur species (Stone et al., 1994). Abiotic reductants capable of reducing chlorinated solvents can be generated via chemical pathways (such as weathering) or microbial pathways (such as microbial respiration) (Rügge et al., 1998, Smolen et al., 2003). Most naturally occurring reductants are thermodynamically capable of reducing the more highly chlorinated solvents, such as PCE, TCE and CT, as shown in the redox ladder presented in Figure 4.4.

The redox ladder is organized by reduction potentials (E_H in volts), which represent a measure of a chemical’s redox reactivity. The reduction potentials in Figure 4.4 have been adjusted to pH 7.0 to reflect conditions more relevant to groundwater aquifers. Large, positive E_H values correspond to species whose reduction is thermodynamically favorable ($\Delta G << 0$; as a convention, E_H values are reported for reduction reactions). Species lower on the ladder (at more negative E_H values) can, from a thermodynamic perspective, reduce species higher on the ladder. The redox ladder reveals that several iron and sulfur species are thermodynamically capable of reducing a wide range of chlorinated solvents at pH 7.0. Figure 4.4 also illustrates that a greater number of chlorines on a solvent tends to result in a more positive E_H value. Thus, highly chlorinated solvents (e.g., CT) can usually be considered more easily reduced than species with a lower number of chlorine substituents (e.g., dichloromethane [DCM]), although exceptions to this generalization exist. The focus of the following discussion will be on the most common reductants for chlorinated solvents, specifically reduced iron species (e.g., iron metal and ferrous iron), reduced sulfur species (hydrogen sulfides and polysulfides) and natural organic matter (NOM).

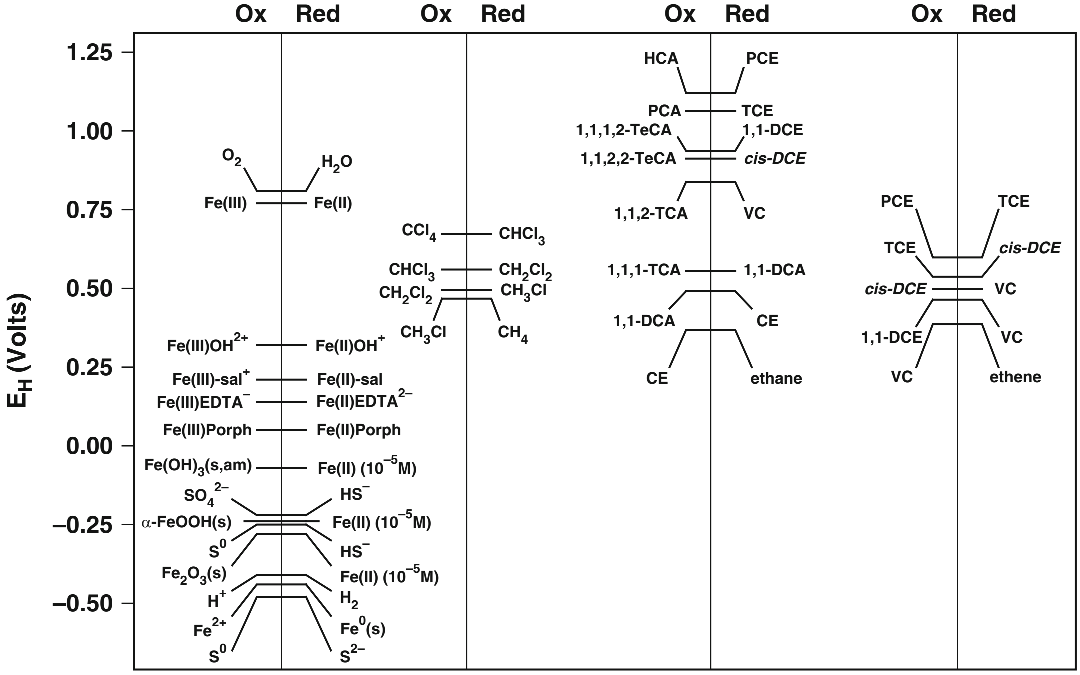


Figure 4.4. Reduction potentials (E_H values) for some environmentally relevant reductants and selected chlorinated solvents. Figure adapted from Schwarzenbach et al., 2003. Unless otherwise noted, E_H values were calculated at pH 7 and a Cl^- concentration of 10^{-3} M. Values of E_H for chlorinated solvents were obtained from Totten and Roberts (2001), while values for reduced iron and sulfur species were taken from Stumm (1992), Haderlein and Pecher (1998) and Bard et al. (1985).

Iron Metal. The majority of work on the abiotic reduction of chlorinated solvents by iron species has focused on zero-valent iron (Fe(0)) because of its use in subsurface permeable reactive barriers (PRBs). A brief introduction to the abiotic reactions involved with iron metal reduction is provided, but the reader is referred to Chapter 16 of this monograph by Gillham et al. for a complete review of the application of Fe(0) to chlorinated solvent remediation.

Iron metal is a strong reductant with a standard reduction potential of -0.44 volts (V). From the redox ladder in Figure 4.4, it is clear that iron metal can thermodynamically reduce most chlorinated solvents. With respect to reduction pathways, it was initially thought that chlorinated solvents were reduced by Fe(0) according to sequential hydrogenolysis pathways (Gillham and O'Hannesin, 1994). For example, the reduction of PCE to ethene via sequential hydrogenolysis is illustrated by the dashed arrows in Figure 4.5.

An obvious disadvantage of dechlorination via sequential hydrogenolysis is the possible formation of vinyl chloride. More recent work, however, has shown that polychlorinated ethenes

(Roberts et al., 1996; Arnold and Roberts, 2000) and ethanes (Arnold et al., 2002; Cwiertny and Roberts, 2005; Song and Carraway, 2005) with vicinal substituents react nearly exclusively via reductive β-elimination. For the chlorinated ethenes included in Figure 4.5, reductive β-elimination (shown using solid arrows) results in the formation of acetylene species that react relatively quickly with Fe(0) to produce fully dechlorinated products such as ethene and ethane.

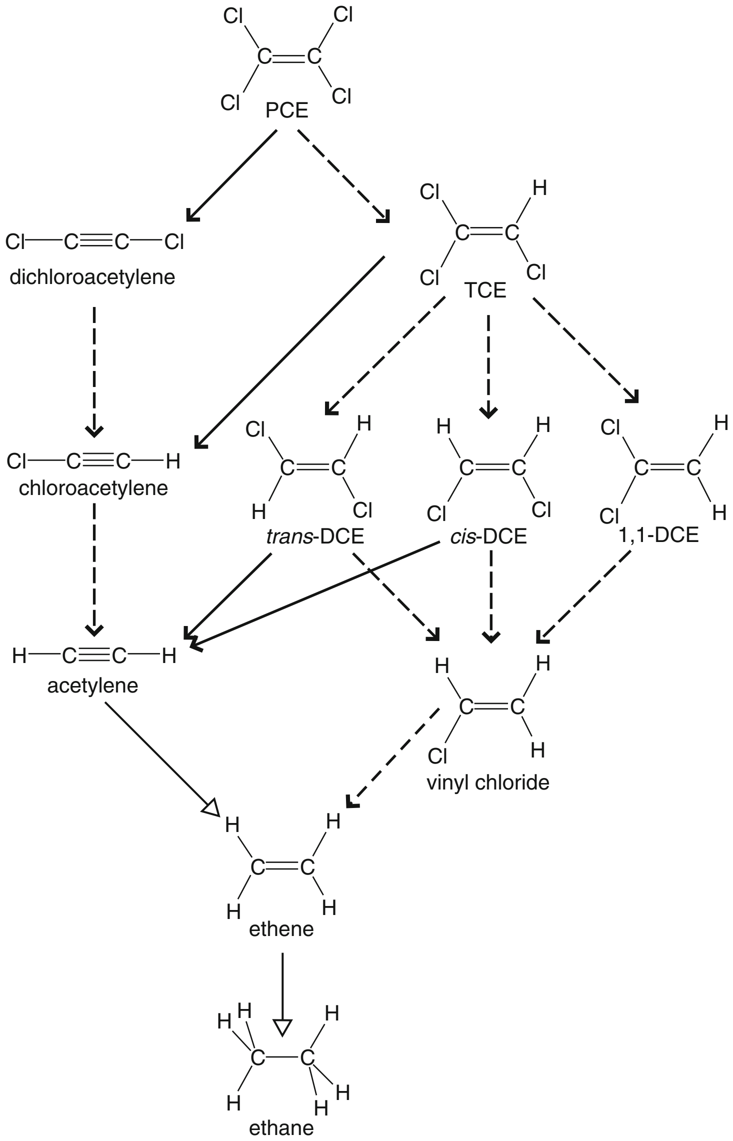


Figure 4.5. Proposed pathways for PCE reduction by Fe(0) (adapted from Arnold and Roberts, 2000). Dashed arrows represent hydrogenolysis pathways, while solid arrows indicate reductive β-elimination reactions, which tend to predominate for most polyhalogenated ethenes in Fe(0) systems. Open arrowheads indicate reductions not involving dehalogenation.

For species with multiple chlorine substituents on only one carbon center (e.g., 1,1,1-TCA), product distributions consistent with α-elimination have been observed. For example the reduction of 1,1-DCE by Fe(0) yielded ethene as the primary reaction product (Roberts et al., 1996; Arnold and Roberts, 2000), and reduction of 1,1,1-TCA yielded products consistent with parallel reductive α-elimination (ethane and ethylene) and hydrogenolysis (1,1-DCA) (Fennelly and Roberts, 1998). Competing α-elimination and hydrogenolysis pathways have also been proposed for CT reduction by Fe(0) (Támara and Butler, 2004).

Despite extensive research focusing on Fe(0) reactivity toward chlorinated solvents, the identity of the relevant reductant remains the topic of some debate. As discussed by Matheson and Tratnyek (1994) and later by Scherer et al. (1998b), numerous electron donors potentially exist in Fe(0) systems. Perhaps the most logical reductant is Fe(0) (Fe(0) → Fe(II) + $2e^-$), which could react with chlorinated solvents either at corrosion pits where it remains exposed to solution (Gaspar et al., 2002), or via the conduction of electrons through the mixed-valent oxide coating that is likely present on the Fe(0) particle surface (Scherer et al., 1998b). Alternatively, products of the corrosion reaction between Fe(0) and water also could be capable of reducing chlorinated solvents. Possible redox active corrosion products include Fe(II), particularly when it is sorbed to the Fe(0) particle surface, and mixed-valent iron oxide phases such as magnetite, green rust and iron carbonate hydroxide, all of which have been observed in column experiments exploring Fe(0) PRB longevity (Kohn et al., 2005). Others have also proposed that reduced forms of atomic hydrogen, which are produced as intermediates during the reduction of water to H_2, represent redox-active agents in Fe(0) systems (Li and Farrell, 2001; Li and Farrell, 2002; Oh et al., 2002).

Ferrous Iron. Several naturally occurring ferrous iron species are thermodynamically capable of reducing many chlorinated solvents. In the subsurface, Fe(II) species may exist as aqueous complexes, sorbed phases, or as part of mineral structures, and all may play a significant role in pollutant reduction (Haderlein and Pecher, 1998; Amonette, 2002). Aqueous Fe(II) at low pH is not a particularly strong reductant with an $E_H^o = 0.77$ V (more than 1,000 millivolts [mV] more positive than Fe(0)). Complexation of Fe(II) with hydroxide ions at higher pH values, however, increases the redox potential, so that aqueous Fe(II)-OH complexes are capable of reducing highly chlorinated solvents. For example, the reduction of HCA and CT by $Fe(II)OH^+$ is thermodynamically favorable at pH 7.0, as illustrated in the redox ladder in Figure 4.4. The few observations of homogeneous reduction of chlorinated solvents by aqueous Fe(II), however, report orders of magnitude slower rates than those observed in the presence of transition metal catalysts or mineral surfaces (e.g., Elsner et al., 2004b; Maithreepala and Doong, 2004).

Numerous laboratory studies have reported heterogeneous reduction of chlorinated solvents by both sorbed Fe(II) phases and structural Fe(II) found in minerals and clays (Haderlein and Pecher, 1998 and references therein). Most of the work conducted with sorbed Fe(II) and structural Fe(II) has been performed in the laboratory with model oxides and clays. Notably, however, several recent studies on the reduction of chlorinated ethenes and methanes by aquifer sediments concluded that Fe(II) species in the form of magnetite (Ferrey et al., 2004) or sorbed (i.e., surface-bound) Fe(II) (Kenneke and Weber, 2003) were the primary reductants.

Fe(II) sorbed on model surfaces, such as Fe oxides and clay minerals, has been shown to reduce chlorinated methanes, such as CT (Amonette et al., 2000; Pecher et al., 2002; Elsner et al., 2004a), and chlorinated ethanes, such as HCA (Elsner et al., 2004b). In an extensive study of a variety of mineral sorbents, Elsner et al. (2004b) found significant differences in rates of HCA reduction by sorbed Fe(II), as shown in Figure 4.6. In general, the fastest surface-area-normalized rates were observed for Fe(II) sorbed on iron sulfides, followed by iron oxides, and then iron carbonate (or siderite, $FeCO_3$) (Elsner et al., 2004b). Interestingly, there are very few reports of chlorinated ethene reduction by sorbed Fe(II). One is the work by Lee and Batchelor (2002a), where quite high concentrations of Fe(II) were used (42.6 millimolar [mM]) and some *cis*-DCE and VC reduction was observed. However, it is likely that the solubility limit for Fe(II) was exceeded in these studies, and redox active Fe(II)-containing solid phases (e.g., green rust, magnetite or ferrous hydroxide) may have formed.

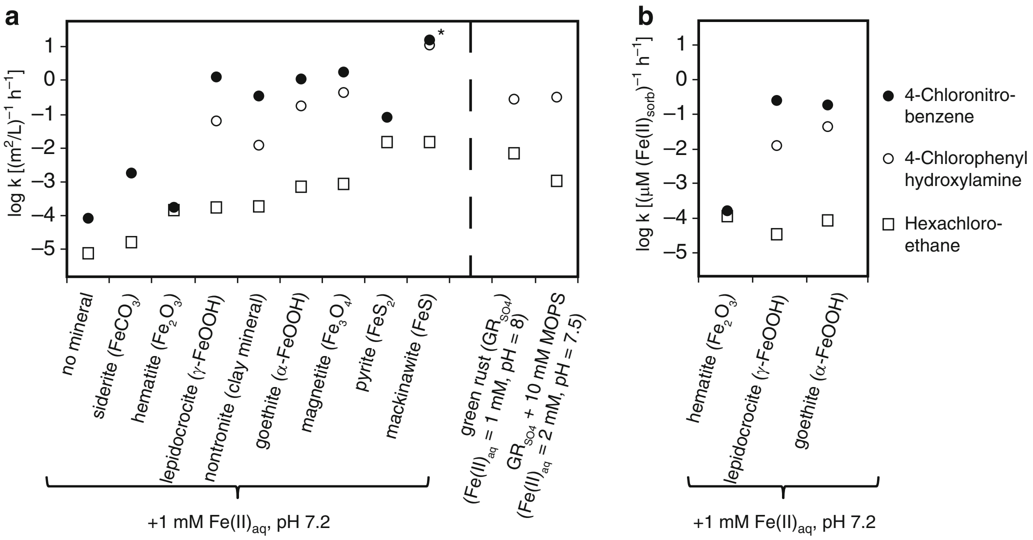


Figure 4.6. Comparison of logarithmic pseudo first-order measured rate coefficients for hexachlorethane reduction by Fe(II) in the presence of a variety of minerals. Open squares are hexachloroethane and reveal a trend of iron sulfides > iron oxides > siderite. Also shown are patterns observed for 4-chloronitrobenzene and 4-chlorophenyl hydroxylamine. Data shown in (a) is surface area-normalized and in (b) is normalized to sorbed Fe(II). The asterisk (*) indicates likely mass transfer limitation. Reproduced from Elsner et al., 2004b (reprinted with permission from the American Chemical Society).

The enhanced reactivity of sorbed Fe(II) is commonly attributed to surface complexation of Fe(II) by hydroxo ligands on the mineral surface, which stabilizes the Fe(III) oxidation state and lowers the Fe(III)-Fe(II) redox potential (Stumm and Morgan, 1996). The sorbed Fe(II) species or phase responsible for contaminant reduction, however, is still unclear. In most cases, the kinetics of contaminant reduction are described as proportional to the concentration of a stable, sorbed Fe(II) species at the mineral surface (determined from the disappearance of Fe(II) from solution). There is growing evidence, however, that both phase transformations and/or electron transfer reactions occur when Fe(II) sorbs on Fe oxides, indicating that the reaction pathways with sorbed Fe(II) are more complex and require additional research (Jeon et al., 2003; Williams and Scherer, 2004; Hansel et al., 2005; Pedersen et al., 2005).

Structural Fe(II) present in Fe(II) or mixed-valent Fe(III)-Fe(II) minerals such as iron sulfides, green rusts and magnetite also have been shown to reduce chlorinated solvents in several laboratory studies. Iron sulfides, such as mackinawite (FeS) and pyrite (FeS_2), have been shown to be very reactive towards most chlorinated solvents (Butler and Hayes, 2002; Hanoch et al., 2006). Both reductive β-elimination and hydrogenolysis have been observed for chlorinated ethene reduction (see Figure 4.5) and there is significant interest in controlling this branching in order to avoid the formation of the toxic VC product (Butler and Hayes, 1999).

Green rusts, which are transient mixed-valent layered double hydroxides composed of $Fe(II)(OH)_2$ and $Fe(III)(OH)_2^+$ (Carrado et al., 1988), have been shown to reduce both halogenated ethanes (O'Loughlin and Burris, 2004) and methanes (Erbs et al., 1999; O'Loughlin et al., 2003). Similar to sorbed Fe(II), there are few reports of chlorinated ethene reduction by green rust, with the exception of two studies where partial reduction of chlorinated ethenes was observed with sulfate green rust and in Fe(II) cement slurries where green rust was expected to form (Hwang and Batchelor, 2000; Lee and Batchelor, 2002b).

One of the more commonly occurring mixed-valent iron oxides, magnetite (Fe_3O_4), has often been studied in the presence of aqueous Fe(II), but "control" experiments with magnetite alone typically result in negligible dechlorination (Pecher et al., 2002). Recently, however, there is evidence that CT can be reduced by structural Fe(II) in chemically synthesized magnetite (Danielsen and Hayes, 2004). In this work, as in several studies with Fe(II) reductants, rates increased significantly over a pH range of 6 to 8.

With respect to chlorinated solvent reactivity and reduction pathways, the reduction of CT by either Fe(II) sorbed on Fe(III) (hydr)oxides or Fe(II)-containing mineral phases has been most extensively investigated (Amonette et al., 2000; Pecher et al., 2002; O'Loughlin et al., 2003; Danielsen and Hayes, 2004; Elsner et al., 2004a; McCormick and Adriaens, 2004). CT reduction is believed to initiate via a single electron transfer that cleaves a C-Cl bond and generates a trichloromethyl radical (Figure 4.7), although alternative pathways have also been proposed (Amonette et al., 2000). The fate of this radical intermediate ultimately determines the products of CT reduction. It could either abstract a hydrogen or undergo an additional one electron transfer followed by protonation to yield chloroform (CF), the hydrogenolysis product that is generally more persistent than CT in reduced iron systems. Alternatively, the trichloromethyl radical could undergo an additional reduction step followed by the loss of a chloride ion to yield dichlorocarbene. This reductive α-elimination pathway is more favorable from a treatment perspective, as it can result in the formation of benign, fully dechlorinated end products such as formate and carbon monoxide (as shown in Figure 4.7). Additionally, further reduction of dichlorocarbene may result in the formation of methane (McCormick and Adriaens, 2004). Variations of the reaction pathway in Figure 4.7 also have been suggested for the reduction of CT by Fe(0) (Támara and Butler, 2004; Nurmi et al., 2005), by HS^- in the presence of mineral surfaces (Kriegman-King and Reinhard, 1991), and by iron sulfides (Kriegman-King and Reinhard, 1994).

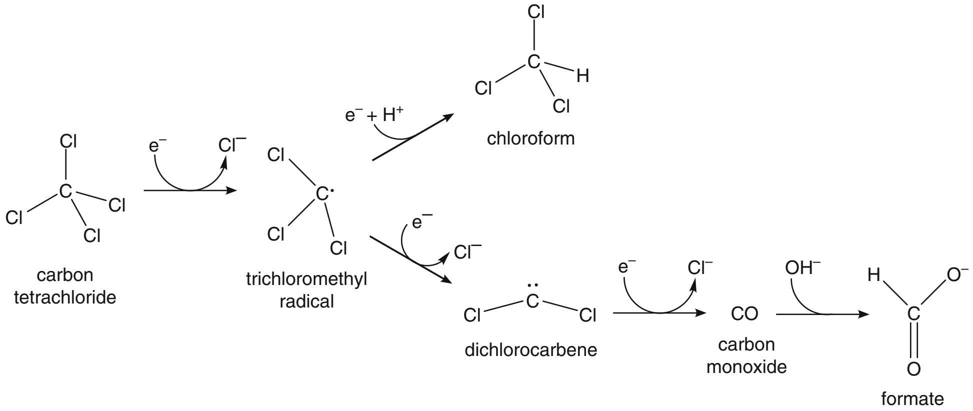


Figure 4.7. Proposed pathways for carbon tetrachloride (CT) reduction by Fe(II) associated with Fe (III) oxide surfaces or Fe(II) containing minerals. Similar reduction pathways also have been proposed for CT reduction in Fe(0) systems (Támara and Butler, 2004), as well as for CT reduction by reduced sulfur species (Kriegman-King and Reinhard, 1992) and vitamin B_{12} (Krone et al., 1991).

Previous investigators have found that several factors can influence the relative rates (or branching ratio) of the hydrogenolysis and reductive α-elimination pathways during CT reduction. For instance Pecher et al. (2002) found that the concentration of CF increased with increasing pH in Fe(II)-containing iron (hydr)oxides systems. The same result was also observed by Danielsen and Hayes (2004) for CT reduction by magnetite. Additional factors that have also been found to influence the relative abundance of CT reduction products include the sorbed concentration of Fe(II) (Pecher et al., 2002), the presence of transition metal additives on the iron mineral surface (O'Loughlin et al., 2003), and the presence of compounds in solution that can provide either hydrogen atoms (Elsner et al., 2004a) or protons (e.g., amine buffers [Danielsen et al., 2005]) that can react with intermediates of CT reduction.

NOM. Natural organic matter, or NOM, can be defined as the structurally diverse mixture of organic macromolecules produced from the decay of terrestrial and aquatic plant matter (Macalady and Ranville, 1998). NOM is traditionally divided into several subclasses based upon its properties. For example, humic substances, which comprise the major organic fraction in soil (Aiken et al., 1985), represent the organic matter that is resistant to further biological decomposition (Macalady and Ranville, 1998). Humic substances are further categorized based upon their aqueous solubilities; humic acid is operationally defined as the fraction that is soluble at high pH values but precipitates at pH 2, whereas fulvic acid is the portion soluble over the entire pH regime (Aiken et al., 1985). As NOM is ubiquitous in both aquatic and terrestrial environments (e.g., the average concentration of dissolved NOM in groundwater is approximately 4 mg carbon/L [Macalady and Ranville, 1998]), its influence on chlorinated solvent fate has been the focus of extensive laboratory investigations.

It is widely accepted that NOM serves as a mediator for the reduction of chlorinated solvents. As shown in Figure 4.8, a mediator facilitates the transfer of electrons between a reductant that is present in excess (referred to as the bulk reductant) and an electron acceptor (in our case, the chlorinated solvent) (Dunnivant et al., 1992). The bulk reductant, typically species such as Fe(II) or HS^-, transfers electrons to the mediator, which in turn serves as the reductant for the chlorinated solvent. The oxidized mediator can then be re-reduced by the bulk reductant, thereby generating a catalytic cycle for chlorinated solvent reduction. Typically, mediators such as NOM are present in relatively low concentrations and do not exhibit considerable reactivity toward chlorinated solvents in the absence of a bulk reductant. Similarly, the bulk reductant also displays only a limited capacity for reducing chlorinated solvents in the absence of a mediator. On the other hand, in systems with both a mediator and a bulk reductant, rates of chlorinated solvent reduction are greater than that anticipated from the summed reactivities of both species.

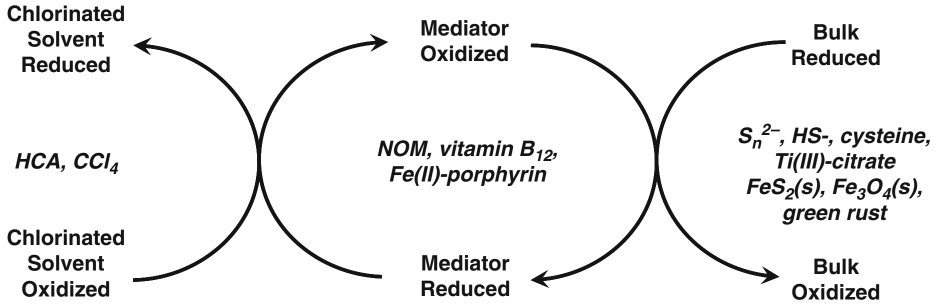


Figure 4.8. Schematic illustrating the catalytic role of mediators for chlorinated solvent reduction, with environmentally relevant examples of each species (adapted from Dunnivant et al., 1992).

The ability of NOM to serve as an electron transfer mediator is often attributed to redox active quinone functional groups (examples of quinone-containing compounds are shown in Figure 4.9) present in its structure (Tratnyek and Macalady, 1989; Schwarzenbach et al., 1990; Dunnivant et al., 1992). For instance, Curtis and Reinhard (1994) examined the reduction of CT and HCA by humic acid in the presence of Fe(II) and HS^-. Consistent with NOM serving as an electron transfer mediator, a 10-fold increase in the rates of CT and HCA reduction was observed in systems containing both a bulk reductant and humic acid. They conducted additional experiments using anthroquinone disulfonic acid (AQDS), which contains a quinone functional group (see Figure 4.9), as a model for structurally complex NOM. Curtis and Reinhard found that the reduced form of AQDS could reduce CT and HCA. Moreover, the pH dependence of the reduction reaction was similar to that observed for the reduction of HCA and CT by humic acid, supporting a role for quinone moieties as the reactive entity in NOM.

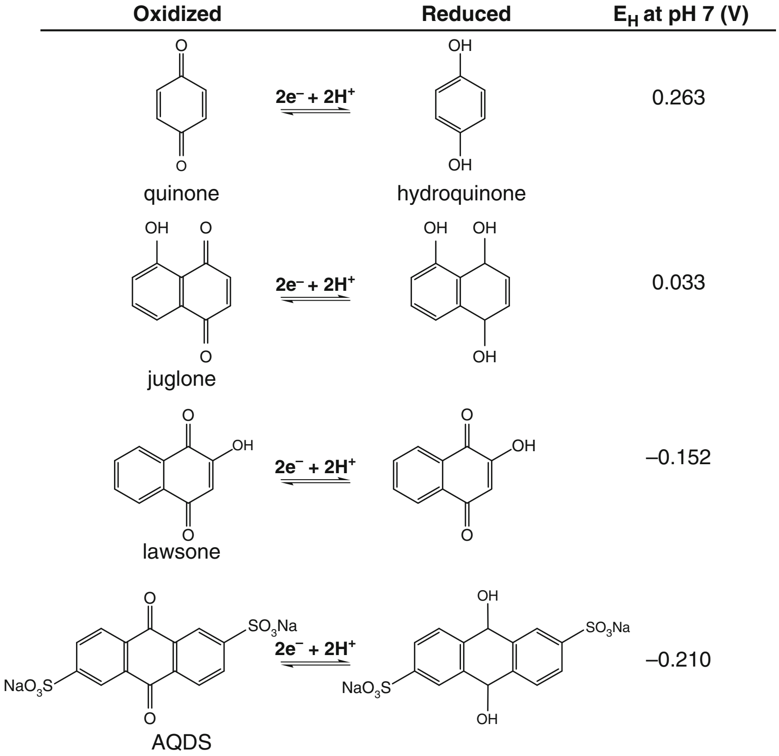


Figure 4.9. Examples of compounds containing a quinone functionality that have been used as models of NOM for mediating chlorinated solvent reduction (adapted from Schwarzenbach et al., 1990). Reduction potentials for each half-reaction are provided, determined at a pH value of 7.

Alternative explanations for the redox activity of NOM have also been proposed. Perlinger et al. (1996) observed that juglone, another model quinone (see Figure 4.9), catalytically reduced HCA in the presence of HS^-, whereas electrochemically reduced juglone was unreactive toward HCA. Based upon these results, the authors proposed that the reactive form of juglone was a product of the addition reaction between juglone and HS^-. A similar hypothesis was suggested in the authors' later works, which examined polychlorinated methane and ethane reduction in juglone/HS^- systems (Perlinger et al., 1998). Subsequent results from additional kinetic and spectroscopic studies (Perlinger et al., 2002) further supported the existence of such a reactive entity in their experimental systems.

It is also possible that complexes between NOM and metal ions play a prominent role in chlorinated solvent reduction. O'Loughlin et al. (1999) examined the reactivity of nine transition metal-humic acid complexes in the presence of the bulk reductant titanium citrate. For Ni complexes, they observed near complete transformation of TCE to ethane and ethene. In fact, later work by this same group (Ma et al., 2001) revealed that Ni complexes with humic acid and NOM were far more efficient as mediators for TCE reduction than quinones, which displayed at best limited reactivity toward TCE.

Although the exact nature of the reactive entities in NOM remains the subject of investigation, NOM must be viewed as a possible reductant for some chlorinated solvents in natural systems. This is particularly true in reducing environments, where reactions with iron and sulfur species, as well microbiological processes (Lovley et al., 1996; Coates et al., 1998), can yield reduced forms of NOM. It also may be necessary to consider the importance of NOM under oxic conditions; recent results of Kappler and Haderlein (2003) indicate that reduced forms of NOM maintain some of their electron donating ability even in the presence of oxygen.

Reduced Sulfur Species. Reduced forms of sulfur represent another possible reductant for chlorinated solvents. These include hydrogen sulfide species (HS^- and H_2S) and polysulfide ions S_n^{2-} (where n refers to the number of sulfur atoms in a polysulfide chain). Each of these species contains sulfur with an oxidation state of −II. For comparison, oxidized forms of sulfur include elemental sulfur (S^0; oxidation state 0), sulfite (SO_3^{2-}; oxidation state of +IV) and sulfate (SO_4^{2-}; oxidation state +VI). Reduced sulfur species are generated from the biologically mediated reduction of sulfate in oxygen-free environments such as those typically encountered in groundwater pollutant plumes.

With respect to their reactivity, reduced sulfur is unique in that it can serve either as a nucleophile in substitution and elimination reactions or as an electron donor for chlorinated solvent reduction. The relative strength of sulfur species as nucleophiles follows the trend $S_n^{2-} > HS^- >> H_2S$ (Barbash and Reinhard, 1989). Based upon the standard reduction potentials in our redox ladder (Figure 4.4), polysulfides are believed to be the strongest reductants. For example, rate constants for the reaction of S^{2-} with HCA, which is proposed to occur predominately via a reductive pathway (Miller et al., 1998), are more than two orders of magnitude greater than rate constants for hydrogen sulfide species (Perlinger et al., 1996). Whether a reduced sulfur species serves as a nucleophile or reductant in reactions with chlorinated solvents will depend upon several factors including the relative abundance of the reduced sulfur species and the chemical identity of the chlorinated solvent.

To date, most investigations have focused on the role of HS^- as a bulk reductant in the catalytically mediated reduction of chlorinated solvents (see Figure 4.8). In experimental systems, natural organic matter (Curtis and Reinhard, 1994), quinone-containing model compounds (Perlinger et al., 1996; Perlinger et al., 1998), and mineral surfaces (Kriegman-King and Reinhard, 1992) serve as catalysts for chlorinated solvent reduction in the presence of HS^-. While reduction of chlorinated solvents by HS^- in the absence of these catalysts has also been observed in these studies, the rates of such reactions are typically much slower. Consequently, it is often assumed that the contribution of direct chlorinated solvent reduction by reduced sulfur species is of relatively little importance in natural systems where redox mediators such as NOM are abundant.

Miller et al. (1998) have suggested, however, that in certain environments the concentrations of reduced sulfur species, particularly polysulfides, can achieve high enough values such that their role as a direct reductant for chlorinated solvents cannot be discounted. They examined the transformation of HCA and PCA in batch systems with water from Mystic Lake, Massachusetts, which contained approximately 7 mM of total hydrogen sulfide species and roughly 80 micromolar (μM) of reactive polysulfide species. Using rate constants for the reaction between reduced sulfur species and HCA calculated by Perlinger et al. (1996) and their own kinetic and product distribution data, they concluded that approximately 20% of HCA disappearance could be attributable to an unmediated reaction between reduced sulfur species and HCA. In particular, polysulfide species were proposed to be the primary reductant. Their results illustrate that in certain environments, microbial sulfate reduction may indeed produce high enough concentrations of reduced sulfur species such that their role as reductants merits consideration.

4.4.3 Reaction Kinetics

The lifetime of chlorinated solvents in subsurface environments will be influenced by the rate at which hydrolysis, dehydrohalogenation, reductive dehalogenation and oxidation reactions occur. If it is assumed that these reactions occur independently of one another and in parallel, a generalized rate expression can be developed. For example, the expression for chloromethane (CM) transformation is as follows:

$$
\begin{aligned}
rate\left(\frac{mol}{L\cdot s}\right) &= -\frac{d[CM]}{dt} \\
&= k_{RED}[RED][CM] + k_{OX}[OX][CM] + k_N[CM] + k_B[OH^-][CM] \qquad \text{(Eq. 4.14)}
\end{aligned}
$$

In this expression, [CM], [OX], and [RED] represent the chloromethane, oxidant, and reducant concentrations, respectively. k_{RED} and k_{OX} are second-order rate coefficients with units of $M^{-1}s^{-1}$ for the reduction and oxidation of CM. If more than one reductant or oxidant species is present, additional rate terms would be needed to account for these parallel redox pathways.

The terms k_{N}[CM] and $k_{\mathrm{B}}[OH^-]$[CM] account for the combined rate of CM hydrolysis and dehydrohalogenation at neutral and basic pH values, respectively. Values of k_{N} (which have units of M^{-1}) and k_{B} (which have units of $M^{-1}s^{-1}$) are determined from laboratory experiments that measure the rate of chlorinated solvent transformation resulting from reaction with H_2O and OH^- over a range of pH values. Values of k_{N} and k_{B} are well established for most chlorinated solvents, and these values are summarized in Table 4.2. Note that for many chlorinated solvents, values of k_{B} are several orders of magnitude greater than values of k_{N}. However, the rate of all base-promoted pathways ($=k_{\mathrm{B}}[OH^-][CM]$) also depends upon the concentration of OH^-, which increases with increasing pH. Thus, for most chlorinated solvents, the rate of the neutral hydrolysis and dehydrohalogenation reactions predominates at neutral pH values, whereas the rate of the base-promoted pathway is typically only significant at higher pH values ($pH \geq 10$).

For practical purposes, Equation 4.14 can be simplified by introducing the concept of a pseudo first-order rate constant or k_{obs} value, which represents a measure of the overall reactivity of CM in the system of interest (Equations 4.15 and 4.16)

$$rate\left(\frac{mol}{L\cdot s}\right) = \frac{d[\mathrm{CM}]}{dt} = -k_{obs}[\mathrm{CM}] \qquad \text{(Eq. 4.15)}$$

where

$$k_{obs}\left(s^{-1}\right) = k_N + k_B[OH^-] + k_{RED}[RED] + k_{OX}[OX] \qquad \text{(Eq. 4.16)}$$

The utility of k_{obs} values (which have units of s^{-1}) is that they are composite rate constants that accounts for all CM transformation pathways, and in many instances are easier to determine experimentally than the individual rate constants for parallel reaction pathways. On the other hand, k_{obs} values are limited in that they are usually only applicable to the conditions under which they were measured, making their extrapolation to other conditions, or even field settings, unreliable.

Table 4.2. Experimental Values of k_N and k_B at 25°C Taken from the Literature for Selected Chlorinated Solvents

Species	k_N (s^{-1})	k_B ($M^{-1}s^{-1}$)	Reference
Methanes			
CM	2.30×10^{-8}	6.50×10^{-6}	Heppolette and Robertson, 1959
DCM	3.20×10^{-11}	2.20×10^{-8}	Moelwyn-Hughes, 1949
CF	3.00×10^{-12}	9.00×10^{-5}	Jeffers et al., 1989
CT	5.00×10^{-10}	NO[a]	Jeffers et al., 1996
Ethanes			
Chloroethane	8.50×10^{-9}	6.5×10^{-5}	Jeffers and Wolfe, 1996
1,2-DCA	3.00×10^{-10}	2.00×10^{-6}	Jeffers and Wolfe, 1996
1,1-DCA	3.80×10^{-10}	1.30×10^{-8}	Jeffers et al., 1989
1,1,1-TCA	2.00×10^{-8}	NO	Haag and Mill, 1988
1,1,2-TCA	9.20×10^{-13}	3.70×10^{-3}	Jeffers et al., 1989; Walraevens et al., 1974[b]
1,1,2,2-TeCA	1.60×10^{-10}	1.6	Jeffers et al., 1989; Haag and Mill, 1988
1,1,1,2-TeCA	4.00×10^{-10}	3.50×10^{-4}	Jeffers and Wolfe, 1996
PCA	8.30×10^{-10}	2.70×10^{1}	Jeffers et al., 1989; Roberts and Gschwend, 1991
HCA	NO	1.30×10^{-10}	Jeffers et al., 1989
Ethenes			
1,1-DCE	NO	1.90×10^{-9}	Jeffers et al., 1989
cis-DCE	NO	1.10×10^{-11}	Jeffers et al., 1989
trans-DCE	NO	1.10×10^{-11}	Jeffers et al., 1989
TCE	NO	1.90×10^{-7}	Jeffers et al., 1989
PCE	NO	2.40×10^{-10}	Jeffers et al., 1989

[a] NO = not observed
[b] references for k_N and k_B, respectively

Integration of Equation 4.15 provides a relationship that describes the change in [CM] as a function of time (t) (Equation 4.17) in which $[CM]_0$ is the initial concentration of chloromethane.

$$[CM] = [CM]_0 e^{-k_{obs}t} \qquad \text{(Eq. 4.17)}$$

According to Equation 4.17, the decrease in CM concentration as a function of time follows an exponential decay, such as the concentration profile illustrated in Figure 4.10. Furthermore, by taking the natural log of the integrated rate expression, the following relationship between ln [CM] and t is obtained.

$$\ln[CM] = \ln[CM]_0 - k_{obs}t \qquad \text{(Eq. 4.18)}$$

From Equation 4.18, a plot of the ln[CM] versus t (shown as an inset in Figure 4.10) should yield a line with a slope of $-k_{obs}$ and a y-axis intercept equal to $\ln[CM]_0$.

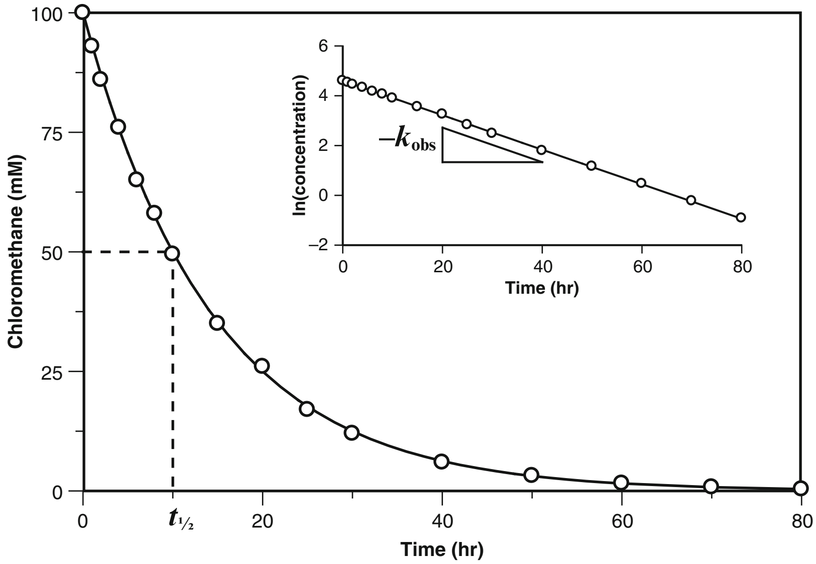


Figure 4.10. Illustration of first-order kinetic behavior for chlorinated solvent degradation in a closed system. The concentration profile follows exponential decay. Dashed lines indicate the half life (or $t_{1/2}$ value) when [CM] = ½[CM]$_0$. Inset shows a first-order plot with the natural logarithm of chlorinated solvent concentration plotted versus time. The slope of such a semi-log plot can be used to determine pseudo first-order rate constants (or k_{obs} values) for chlorinated solvent transformation.

An additional benefit of k_{obs} values is that they can be used to estimate the half life (or $t_{1/2}$ value) of a chlorinated solvent in groundwater. Values of $t_{1/2}$ are defined as the time required for the pollutant concentration in a system to decrease to half of its initial value (the value of $t_{1/2}$ in Figure 4.10 is indicated). Half lives for chlorinated solvents are determined by integrating Equation 4.15 and solving for t when [CM] = ½[CM]$_0$. The result is as follows, where larger k_{obs} values produce shorter half lives.

$$t_{1/2} = \frac{0.693}{k_{obs}} \qquad \text{(Eq. 4.19)}$$

From our expression for k_{obs} (Equation 4.16), it should be clear that values of $t_{1/2}$ for CM (and several other chlorinated solvents) will depend on pH. Specifically, the rate of CM reaction with OH$^-$ will increase with pH, as, by definition, the concentration of OH$^-$ must also be increasing. If oxidation and reduction reactions are neglected, the relationship between chlorinated solvent half life and solution pH can be determined from the published values of k_N and k_B in Table 4.2. The half lives of select chlorinated solvents estimated in this manner over the pH range of 5-10 are shown in Figure 4.11. As Figure 4.11 illustrates, $t_{1/2}$ values for CT and 1,1,1-TCA are independent of pH. This behavior is consistent with the lack of base-promoted reaction pathways for these species. In contrast, values of $t_{1/2}$ estimated for TCE, 1,1,2,2-TeCA, PCA and CF vary considerably over the pH range considered, indicating that these species are able to react with OH$^-$. A change from pH-independent to pH-dependent $t_{1/2}$ values, such as that observed for CF near pH 6, indicates the approximate pH value at which the contributions from reactions with OH$^-$ become significant.

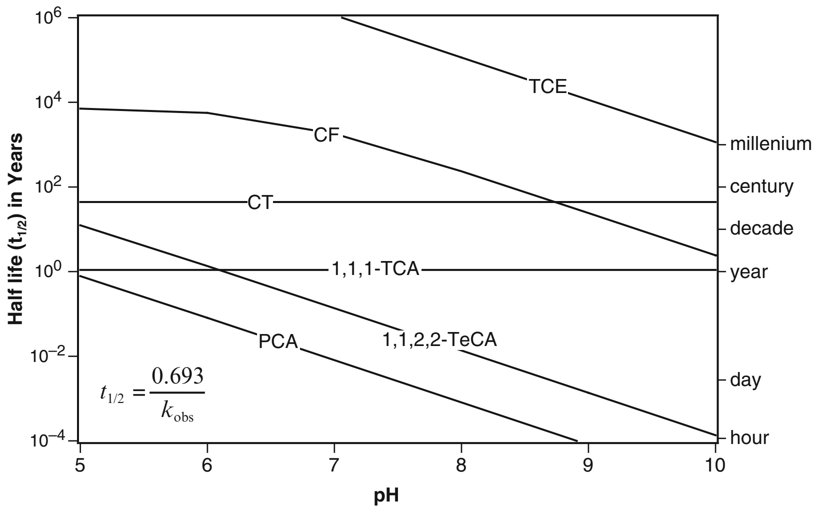


Figure 4.11. Estimated half lives as a function of pH for selected chlorinated solvents undergoing hydrolysis and/or hydrodehalogenation. Half lives were calculated from estimated $k_{obs} = k_N + k_B [OH^-]$ with k_N and k_B values provided in Table 4.2.

The data in Figure 4.11 also suggest that the transformation of chlorinated ethenes by hydrolysis/dehydrohalogenation reactions is relatively unimportant in most environmental systems. The estimated half life for TCE in groundwater at pH 7 is nearly one million years, illustrating why treatment strategies utilizing redox processes (e.g., Fe(0) permeable reactive barriers) are necessary in order to remediate subsurface environments contaminated with chlorinated ethenes. On the other hand, $t_{1/2}$ values for 1,1,2,2-TeCA and PCA are on the order of several days at pH 7. In fact, the dependence of their $t_{1/2}$ values on pH suggests that base-promoted dehydrohalogenation is the predominant reaction pathway over the entire pH range considered, even though the concentration of OH^- is very low for pH values less than 7. The prevalence of the base-promoted dehydrohalogenation of 1,1,2,2-TeCA (to generate TCE) and PCA (to generate PCE) is due primarily to the acidic hydrogen substituents on each compound.

4.4.4 Estimating Rates of Abiotic Transformations

Given the prominent role of chlorinated solvent reductive dehalogenation in both naturally occurring and engineered reductant systems, a method for predicting the reactivity of these contaminants that does not require exhaustive laboratory investigation is desirable. Quantitative structure activity relationships (QSARs), which correlate chlorinated solvent reactivity with molecular properties expected to influence reactivity, are one such predictive tool.

QSARs, also referred to as LFERs, are developed for a class of compounds (e.g., chlorinated methanes, ethanes or ethenes) to explore the influence of structural differences (e.g., the degree of chlorine substitution) on reactivity (Tratnyek et al., 2003). The dependent variable in the relationship, also referred to as the response variable (Tratnyek et al., 2003), is typically a measure of chlorinated solvent reactivity. Common response variables include pseudo first-order rate constants (k_{obs} values with units s^{-1}), surface-area-normalized rate constants (k_{SA} values with units $Lm^{-2}s^{-1}$), or second-order rate constants (k values with units $M^{-1}s^{-1}$). The independent variable, or descriptor variable, is a chemical property of the chlorinated solvent that is expected to influence its reactivity. For example, molecular descriptors commonly used for chlorinated solvent reduction include one- and two-electron reduction potentials (E_1 and E_2, respectively) (Scherer et al., 1998a; Arnold et al., 1999; Lien and Zhang, 2005; Song and Carraway, 2005), the lowest unoccupied molecular orbital energy (E_{LUMO}) (Scherer et al., 1998a; Perlinger et al., 2000; Miehr et al., 2004; Song and Carraway, 2005) and carbon-halogen homolytic bond dissociation energies (D_{RX}) (Liu et al., 2000; Perlinger et al., 2000; Lien and Zhang, 2005).

Table 4.3. Selected QSARs Developed for the Abiotic Reduction of Chlorinated Solvents (adapted from Tratnyek et al., 2003)

Reductant System	Halogenated Solvent Class	QSAR[a]	R^2	Reference
Fe(0)	Methanes, ethanes and ethenes	$\log(k_{SA}) = -1.5(\pm0.1)\cdot E_{LUMO} - 5.7(\pm0.2)$	0.83	Scherer et al., 1998a
Fe(0)	Reductive β–elimination of ethenes	$\log(k_S S_t) = -15(\pm15)\cdot E_2 + 6(\pm8)$	0.71[b]	Arnold & Roberts, 2000
Fe(0)	Hydrogenolysis of ethenes	$\log(k_S S_t) = -31(\pm29)\cdot E_2 + 18(\pm17)$	0.86[b]	Arnold & Roberts, 2000
Fe(0)	CT, TCE plus other model contaminants	$\log(k_{SA}) = -26(\pm12^{c})\cdot E_{LUMO} + 4(\pm1.3^{c})$	0.77	Miehr et al., 2004
Iron-reducing sediments	Methanes	$\log(k_{obs}) = -0.081(\pm0.007\ ^{c})\cdot D_{RX} - 0.036(\pm0.005\ ^{c})\cdot\Delta G^{\circ\prime} + 18.51$	0.97	Kenneke & Weber, 2000
Sulfate-reducing sediments	Methanes	$\log(k_{obs}) = -0.089(\pm0.011\ ^{c})\cdot D_{RX} - 0.029(\pm0.008\ ^{c})\cdot\Delta G^{\circ\prime} + 20.64$	0.94	Kenneke & Weber, 2000
Fe(II) on goethite	Methanes	$\log(k_{obs}) = -0.052(\pm0.013\ ^{c})\cdot D_{RX} - 0.028(\pm0.015\ ^{c})\cdot\Delta G^{\circ\prime} + 12.03$	0.78	Kenneke & Weber, 2000
FeS	Methanes	$\log(k_{obs}) = -0.034(\pm0.016)\cdot D_{RX} - 8.8(\pm4.9)$	0.82	Butler & Hayes, 2000
Fe(II) porphyin/ cysteine	Methanes and ethanes	$\log(k) = -0.08(\pm0.01\ ^{c})\cdot\Delta G^{\circ\prime} + 2.7(\pm0.5\ ^{c})$	0.96	Perlinger et al., 2000
Juglone/H_2S	Methanes and ethanes	$\log(k) = -0.10(\pm0.05\ ^{c})\cdot\Delta G^{\circ\prime} - 0.2(\pm1\ ^{c})$	0.88	Perlinger et al., 2000

[a] Unless otherwise noted, uncertainties in QSAR coefficients represent one standard deviation.
[b] Represents an R^2 value adjusted for degrees of freedom. [c] Uncertainty represents 95% confidence interval.

Examples of QSARs developed for the reduction of chlorinated solvents in several environmentally relevant systems are shown in Table 4.3. Scherer et al. (1998a) developed linear relationships for the reduction of several chlorinated methanes, ethanes and ethenes using k_{SA} values compiled from previously published investigations (Johnson et al., 1996). Their strongest LFER, included in Table 4.3 and shown in Figure 4.12, was that developed using E_{LUMO} values calculated using computational methods. In a more recent study, QSARs developed by Miehr et al. (2004) included not only the chlorinated solvents CT and TCE, but also several other pollutants including metal cations, metal anions and additional organic compounds. They found that relationships between k_{SA} values and computationally derived E_{LUMO} values reasonably described the reduction of all pollutants by Fe(0) even though a broad range of compounds from different chemical classes was considered. Kenneke and Weber (2000) developed QSARs for the reduction of polyhalogenated methanes in iron-reducing and sulfate-reducing sediments, as well as for their reduction by Fe(II) associated with goethite surfaces. They also presented relationships for polyhalogenated methane reduction by iron sulfides, as did Butler and Hayes (2000) for the reduction of halogenated methanes and ethanes. The practical value of these and other QSARs is that the reactivity of compounds that were not used in the construction of the correlation can be predicted so long as the descriptor variable for that compound is known. It is thought (Tratnyek et al., 2003) that the predictive capabilities afforded by QSARs could be helpful in regulatory decision making processes regarding effective cleanup strategies at hazardous waste sites.

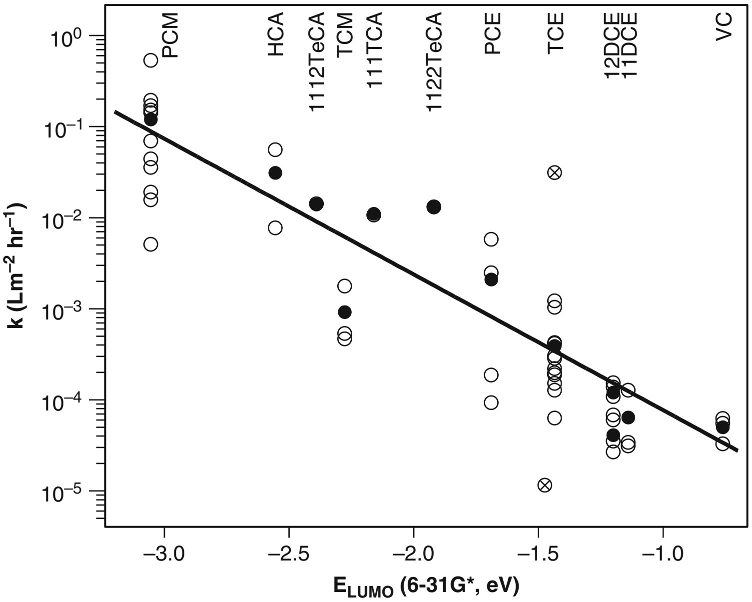


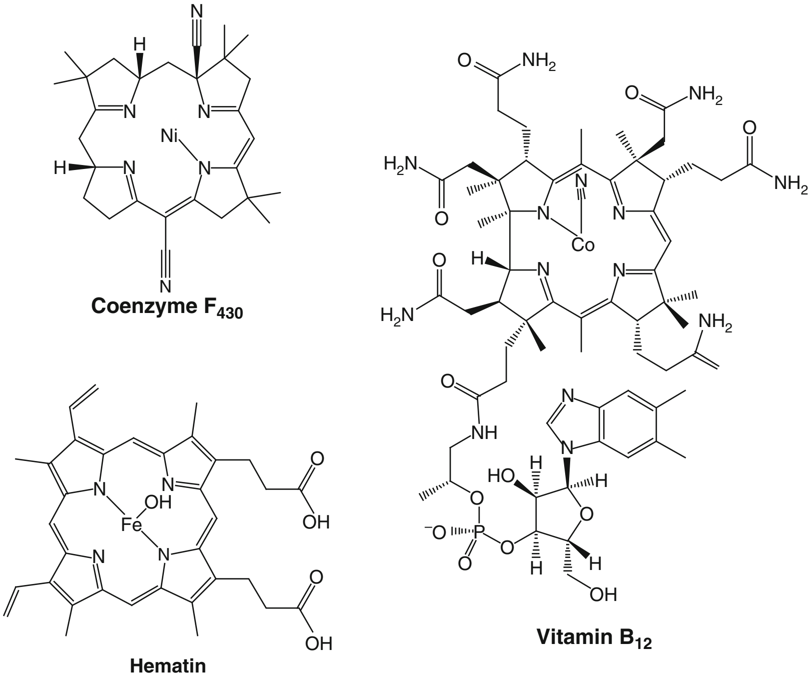
Figure 4.12. Linear free energy relationship for the reduction of chlorinated solvents by Fe(0) constructed by Scherer et al. (1998a). Kinetic data was compiled from rate constants reported in the literature by Johnson et al. (1996), whereas values for the descriptor variable (E_{LUMO}) were determined via computational methods. Reproduced from Scherer et al., 1998a (reprinted with permission from the American Chemical Society).

4.5 COUPLED BIOTIC-ABIOTIC PROCESSES

Although it is appealing to try to separate abiotic and biotic processes, in reality biogeochemical processes are complex and often difficult to decouple. Microbes modify their surrounding chemical environment by respiring to gain energy and assimilating materials to grow. These processes result in modification of both the aqueous and surface chemistry, which can dramatically influence the rate of chlorinated solvent transformation. Here, two examples of coupled biotic-abiotic processes that have been shown to influence chlorinated solvent transformations will be discussed: (1) excretion of reactive extracellular agents and (2) formation of reactive biominerals.

4.5.1 Biocatalysis

In anaerobic environments, bacteria have been shown to degrade chlorinated solvents such as TCE and PCE via a reductive dehalogenation mechanism (see Chapters 3 and 10). In most instances, these biologically-mediated dechlorination reactions appear to be cometabolic processes (Chiu and Reinhard, 1996), meaning that the bacteria do not directly benefit from the reaction. Rather, the chlorinated solvents are reduced by nonselective reagents that are produced by the bacteria for other metabolic functions. It is widely accepted that the reactive agents in these reductive dechlorination reactions are macromolecular metal-organic complexes called metallocoenzymes that are produced by the anaerobic bacteria. Examples of some common metallocoenzymes that react with chlorinated solvents are presented in Figure 4.13 (Gantzer and Wackett, 1991). Each contains a transition metal center that will serve as an electron donor when the metal is present in its reduced form. Thus, the reactive forms of vitamin B_{12} contain a Co(I) or Co(II) center, whereas the fully oxidized Co(III) is unreactive. Similarly, the reactive version of hematin and coenzyme F430 will contain Fe(II) and Ni(I), respectively.



Coenzyme F_{430}

Hematin

Vitamin B_{12}

Figure 4.13. Chemical structures of metallocoenzymes known to function as mediators for chlorinated solvent reduction in the presence of a bulk reductant (after Gantzer and Wackett 1991).

These metallocoenzymes serve as mediators for chlorinated solvent reduction, playing a similar role to other mediators previously described in this chapter (e.g., NOM). Accordingly, metallocoenzymes are typically present in low concentrations in natural environments and require a bulk reductant for the dechlorination reaction to be sustained. The bulk reductant itself is not particularly reactive toward the chlorinated solvent, although it can play an important role in chlorinated solvent reduction. For example, Chui and Reinhard (1995, 1996) found that the identity of the bulk reductant (either titanium[III] citrate or cysteine) influenced the rate and product distribution of CT reduction.

Vitamin B_{12}, which is also referred to as cobalamin, represents perhaps the most commonly studied metalloconenzyme with respect to chlorinated solvent reduction. Cobalamin possesses E_H values of approximately -0.6 and 0.2 V at pH 7 for the reduction of its metal center from Co (II) to Co(I) and Co(III) to Co(II), respectively. In the presence of a bulk reductant, cobalamin can reduce chlorinated methanes (Krone et al., 1989, 1991), ethanes (Schanke and Wackett, 1992) and ethenes (Gantzer and Wackett, 1991; Glod et al., 1997a, 1997b). Generally, its reactivity within a class of chlorinated solvent increases with the number of chlorine substituents (Krone et al., 1989; Gantzer and Wackett, 1991). In fact, interest in the field-scale application of vitamin B_{12} and other metallocoenzymes for the treatment of chlorinated solvents stems primarily from their ability to degrade CT and PCE, which unlike lesser chlorinated compounds are recalcitrant to biodegradation in aerobic environments (Fetzner and Lingens, 1994). With respect to degradation pathways, chlorinated ethenes are proposed to react via parallel hydrogenolysis and reductive β-elimination pathways shown in Figure 4.5 (Burris et al., 1996), whereas CT reduction is analogous to that shown in Figure 4.7 (Krone et al., 1991).

4.5.2 Biominerals

Microbial modification of chemical environments often leads to the formation of inorganic minerals through a process known as biomineralization (Banfield and Nealson, 1997). General trends in both microbial communities and iron mineralogy are illustrated in Figure 4.14 for a sequence of redox zones starting with an oxidizing (aerobic) zone and moving through nitrate-, iron-, sulfate-reducing and methanogenic anaerobic zones. Both Fe(III) and sulfate represent terminal electron acceptors in many aquifers and sediments resulting in formation of reduced iron and sulfur minerals that can reduce chlorinated solvents (Kenneke and Weber, 2003). The change in subsurface iron chemistry is largely a direct result of dissimilatory iron-reducing bacteria (DIRB), that couple the oxidation of organic matter or H_2 to the reduction of Fe(III) to obtain energy for growth (Lovley, 1991; Nealson and Myers, 1992). Biominerals commonly observed include siderite ($FeCO_3$), magnetite (Fe_3O_4), vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$), green rust and maghemite (γ-Fe_2O_3) (Fredrickson et al., 1998; Zachara et al., 2002). In more reducing zones, sulfate-reducing bacteria (SRB) dominate and the production of sulfide from sulfate reduction results in the commonly observed “black” iron sulfides, such as mackinawite (Rickard, 1969).

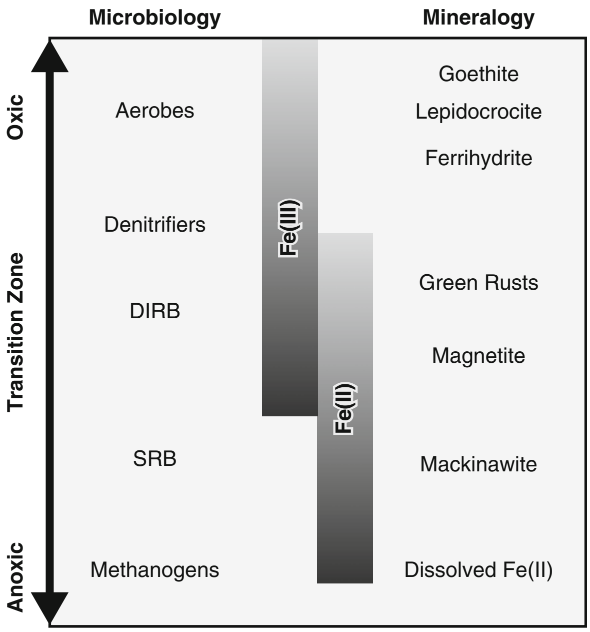


Figure 4.14. Conceptual diagram of dominant microbial-mineral redox zones in the subsurface. Figure originally drawn by Aaron G.B. Williams

The reduction of chlorinated solvents by the chemically synthesized versions of these minerals has been investigated quite extensively (see Section 4.4.2), but fewer studies have measured dechlorination rates in the presence of anaerobes, such as DIRB, SRB and methanogens. Recent work by McCormick et al. (2002, 2004), for example, demonstrated CT reduction by magnetite particles formed from reduction of hydrous ferric oxide by the DIRB species *Geobacter metallireducens*. Interestingly, abiotic rates of reduction by the biomineralized, washed magnetite were found to be significantly faster than the biotic reaction in the presence of cells alone (McCormick et al., 2002; McCormick and Adriaens, 2004).

Gander et al. (2002) have also studied the reduction of 1,1,1-TCA in the presence of FeS and a methanogenic consortium enriched on lactate (Gander et al., 2002). They observed a synergistic effect in the rate of 1,1,1-TCA transformation when FeS and methanogenic consortia were combined that could not be explained by summing the independently measured abiotic and biotic rates. They also found that the supernatant from the cell culture could reduce 1,1,1-TCA, similar to an earlier observation with CT and CF reduction by the supernatant from a pure methanogen culture (Novak et al., 1998). In both cases, soluble, extracellular products appear to react with the chlorinated solvents, but Gander et al. (2002) speculated that the extracellular products may also enhance the reactivity of the FeS by altering the surface redox chemistry. The synergistic interaction observed between FeS and the methanogenic consortium suggests that considering independently determined biotic and abiotic rates may not be sufficient for characterizing rates of chlorinated solvents and that more work is needed to understand coupled abiotic-biotic pathways.

REFERENCES

Aiken GR, McKnight DM, Wershaw RL, MacCarthy P. 1985. An Introduction to Humic Substances in Soil, Sediment and Water. In Aiken GR, McKnight DM, Wershaw RL, MacCarthy P, eds, Humic Substances in Soil, Sediment and Water. John Wiley and Sons, New York, NY, USA, pp 1–9.

Allen-King RM, Groenevelt H, Warren CJ, Mackay DM. 1996. Non-linear chlorinated-solvent sorption in four aquitards. J Contam Hydrol 22:203–221.

Allen-King RM, Grathwohl P, Ball WP. 2002. New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks. Adv Water Resour 25:985–1016.

Allen-King RM, Divine DP, Robin MJL, Alldredge JR, Gaylor DR. 2006. Spatial distributions of perchlorethylene reactive transport parameters in the Borden Aquifer. Water Resour Res 42:1–13.

Amonette JE. 2002. Iron redox chemistry of clays and oxides: Environmental applications. In Fitch A, ed, Electrochemistry of Clays, Vol 10. Clay Minerals Society, Aurora, CO, USA.

Amonette JE, Workman DJ, Kennedy DW, Fruchter JS, Gorby YA. 2000. Dechlorination of carbon tetrachloride by Fe(II) associated with goethite. Environ Sci Technol 34:4606–4613.

Arnold WA, Roberts AL. 2000. Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. Environ Sci Technol 34:1794–1805.

Arnold WA, Ball WP, Roberts AL. 1999. Polychlorinated ethane reaction with zero-valent zinc: Pathways and rate control. J Contam Hydrol 40:183–200.

Arnold WA, Winget P, Cramer CJ. 2002. Reductive dechlorination of 1,1,2,2-tetrachloroethane. Environ Sci Technol 36:3536–3541.

Ball WP, Roberts PV. 1991. Long-term sorption of halogenated organic chemicals by aquifer material. 1. Equilibrium. Environ Sci Technol 25:1223–1237.

Banfield JF, Nealson KH, eds. 1997. Geomicrobiology: Interactions Between Microbes and Minerals. Mineralogical Society of America, Washington, DC, USA.

Barbash JE, Reinhard M. 1989. Reactivity of sulfur nucleophiles toward halogenated organic compounds in natural waters. In Saltzman ES and Cooper WJ, eds, Biogenic Sulfur in the Environment, Vol 393. American Chemical Society, Washington, DC, USA, pp 101–138.

Bard AJ, Parsons R, Jordan J. 1985. Standard Potentials in Aqueous Solutions. Marcel Dekker, New York, NY, USA.

Batterman S, Kulshrestha A, Cheng HY. 1995. Hydrocarbon vapor transport in low moisture soils. Environ Sci Technol 29:171–180.

Brusseau ML. 1994. Transport of reactive contaminants in heterogeneous porous media. Rev Geophys 32:285–313.

Burris DR, Delcomyn CA, Smith MH, Roberts AL. 1996. Reductive dechlorination of tetrachloroethylene and trichloroethylene catalyzed by vitamin B_{12} in homogeneous and heterogeneous systems. Environ Sci Technol 30:3047–3052.

Butler EC, Hayes KF. 1999. Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide. Environ Sci Technol 33:2021–2027.

Butler EC, Hayes KF. 2000. Kinetics of the transformation of halogenated aliphatic compounds by iron sulfide. Environ Sci Technol 34:422–429.

Butler EC, Hayes KF. 2002. Reductive transformation of halogenated aliphatic pollutants by iron sulfide. In Lipnick RL, Mason RP, Phillips ML, Pittman CU, eds, Chemicals in the Environment, Vol 806. American Chemical Society, Washington, DC, USA, pp 113–129.

Carrado KA, Kostapapas A, Suib SL. 1988. Layered double hydroxides (LDHs). Solid State Ionics 26:77–86.

Carroll FA. 1998. Perspectives on Structure and Mechanism in Organic Chemistry. Brooks/Cole, New York, NY, USA.

Chiou CT, Kile DE. 1998. Deviations from sorption linearity on soils of polar and nonpolar organic compounds at low relative concentrations. Environ Sci Technol 32:338–343.

Chiou CT, Porter PE, Schmedding DW. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. Environ Sci Technol 17:227–231.

Chiu PC, Reinhard M. 1995. Metallocoenzyme mediated reductive transformation of carbon tetrachloride in titanium(III) citrate aqueous solution. Environ Sci Technol 29:595–603.

Chiu PC, Reinhard M. 1996. Transformation of carbon tetrachloride by reduced vitamin B_{12} in aqueous cysteine solution. Environ Sci Technol 30:1882–1889.

Coates JD, Ellis DJ, Blunt-Harris EL, Gaw CV, Roden EE, Lovely DR. 1998. Recovery of humic-reducing bacteria from a diversity of environments. Appl Environ Microbiol 64:1504–1509.

Conant BH, Gillham RW, Mendoza CA. 1996. Vapor transport of trichloroethylene in the unsaturated zone: Field and numerical modeling investigations. Water Resour Res 32:9–22.

Curtis GP, Reinhard M. 1994. Reductive dehalogenation of hexachlorethane, carbon tetrachloride, and bromoform by anthrahydroquinone disulfonate and humic acid. Environ Sci Technol 28:2393–2401.

Cwiertny DM, Roberts AL. 2005. On the nonlinear relationship between k_{obs} and reductant mass loading in iron batch systems. Environ Sci Technol 39:8948–8957.

Danielsen KM, Hayes KF. 2004. pH dependence of carbon tetrachloride reductive dechlorination by magnetite. Environ Sci Technol 38:4745–4752.

Danielsen KM, Gland JL, Hayes KF. 2005. Influence of amine buffers on carbon tetrachloride reductive dechlorination by the iron oxide magnetite. Environ Sci Technol 39:756–763.

Dunnivant FM, Schwarzenbach RP, Macalady DL. 1992. Reduction of substituted nitrobenzenes in aqueous solutions containing natural organic matter. Environ Sci Technol 26:2133–2141.

Elsner M, Haderlein S, Kellerhals T, Luzi S, Zwank L, Werner A, Schwarzenbach RP. 2004a. Mechanisms and products of surface-mediated reductive dehalogenation of carbon tetrachloride by Fe(II) on goethite. Environ Sci Technol 38:2058–2066.

Elsner M, Schwarzenbach RP, Haderlein S. 2004b. Reactivity of Fe(II)-bearing minerals toward reductive transformation of organic contaminants. Environ Sci Technol 38:799–807.

Erbs M, Hansen HCB, Olsen CE. 1999. Reductive dechlorination of carbon tetrachloride using iron(II) iron(III) hydroxide sulfate (green rust). Environ Sci Technol 33:307–311.

Fells I, Moelwyn-Hughes EA. 1958. The kinetics of the hydrolysis of methylene dichloride. J Chem Soc 1958:1326–1333.

Fells I, Moelwyn-Hughes EA. 1959. The kinetics of the hydrolysis of the chlorinated methanes. J Chem Soc 1959:398–409.

Fennelly JP, Roberts AL. 1998. Reaction of 1,1,1-trichloroethane with zero-valent metals and bimetallic reductants. Environ Sci Technol 32:1980–1988.

Ferrey M, Wilkin R, Ford R, Wilson J. 2004. Nonbiological removal of cis-dichloroethylene and 1,1-dichlorethylene in aquifer sediment containing magnetite. Environ Sci Technol 38: 1746–1752.

Fetter CW. 1999. Contaminant Hydrogeology. Prentice-Hall, Inc., Upper Saddle River, NJ, USA.

Fetzner S, Lingens F. 1994. Bacterial dehalogenases- biochemistry, genetics and biotechnological applications. Microbiol Rev 58:641–685.

Fredrickson JK, Zachara JM, Kennedy DW, Dong H, Onstott TC, Hinman NW, Li S. 1998. Biogenic iron mineralization accompanying dissimilatory reduction of hydrous ferric oxide by groundwater bacterium. Geochim Cosmochim Acta 62:3239–3257.

Gander JW, Parkin GF, Scherer MM. 2002. Kinetics of 1,1,1-trichloroethane transformation by iron sulfide and a methanogenic consortium. Environ Sci Technol 36:4540–4546.

Gantzer CJ, Wackett LP. 1991. Reductive dechlorination catalyzed by bacterial transition-metal coenzymes. Environ Sci Technol 25:715–722.

Gaspar DJ, Lea AS, Engelhard MH, Baer DR, Miehr R, Tratnyek PG. 2002. Evidence for localization of reaction upon reduction of carbon tetrachloride by granular iron. Langmuir 18:7688–7693.

Gillham RW, O'Hannesin SF. 1994. Enhanced degradation of halogenated aliphatics by zero-valent iron. Ground Water 32:958–967.

Glod G, Angst W, Holliger C, Schwarzenbach RP. 1997a. Corrinoid-mediated reduction of tetrachloroethene, trichloroethene, and trichlorofluoroethene in homogeneous aqueous solution: Reaction kinetics and reaction mechanisms. Environ Sci Technol 31:253–260.

Glod G, Brodmann U, Schwarzenbach RP. 1997b. Cobalamin-mediated reduction of cis- and trans-dichloroethene, 1,1-dichloroethene, and vinyl chloride in homogeneous aqueous solution: Reaction kinetics and mechanistic considerations. Environ Sci Technol 31: 3154–3160.

Grathwohl P. 1990. Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implications on K_{oc} correlations. Environ Sci Technol 24:1687–1693.

Haag W, Mill T. 1988. Effects of a subsurface sediment on hydrolysis of haloalkanes and epoxides. Environ Sci Technol 22:658–663.

Haderlein SB, Pecher K. 1998. Pollutant reduction in heterogeneous Fe(II)/Fe(III) systems. In Grundl T and Sparks D, eds, Mineral-Water Interfacial Reactions: Kinetics and

Mechanisms, ACS (American Chemical Society) Symposium Series 715. ACS, Washington, DC, USA, pp 342–357.

Hanoch RJ, Shao H, Butler EC. 2006. Transformation of carbon tetrachloride by bisulfide treated goethite, hematite, magnetite, and kaolinite. Chemosphere 63:323–334.

Hansel CM, Benner SG, Fendorf S. 2005. Competing Fe(II)-induced mineralization pathways of ferrihydrite. Environ Sci Technol 39:7147–7153.

Heppolette RL, Robertson RE. 1959. Neutral hydrolysis of methyl halides. In Proceedings, Royal Society of London Series A, Mathematical and Physical Sciences 252:273–285.

Heyse E, Augustinj D, Rao P, Defino J. 2002. Nonaqueous phase liquid dissolution and soil organic matter sorption in porous media: Review of system similarities. Crit Rev Environ Sci Technol 32:337–397.

Hwang I, Batchelor B. 2000. Reductive dechlorination of tetrachloroethylene by Fe(II) in cement slurries. Environ Sci Technol 34:5017–5022.

Jeffers PM, Wolfe NL. 1996. Homogeneous hydrolysis rate contstants. Part II: Additions, corrections and halogen effects. Environ Toxicol Chem 15:1066–1070.

Jeffers PM, Ward LM, Woytowitch LM, Wolfe NL. 1989. Homogeneous hydrolysis rate constants for selected chlorinated methanes, ethanes, ethenes and propanes. Environ Sci Technol 23:965–969.

Jeffers PM, Brenner C, Wolfe NL. 1996. Hydrolysis of carbon tetrachloride. Environ Toxicol Chem 15:1064–1065.

Jellali S, Benremita H, Muntzer P, Razakarisoa O, Schafer G. 2003. A large-scale experiment on mass transfer of trichloroethylene from the unsaturated zone of a sandy aquifer to its interfaces. J Contam Hydrol 60:31–53.

Jeon B-H, Dempsey BA, Burgos W. 2003. Kinetics and mechanisms for reactions of Fe(II) with iron(III) oxides. Environ Sci Technol 37:3309–3315.

Jeong S, Werth CJ. 2005. Evaluation of methods to obtain geosorbent fractions enriched in carbonaceous materials that affect hydrophobic organic chemical sorption. Environ Sci Technol 39:3279–3288.

Johnson TL, Scherer MM, Tratnyek PG. 1996. Kinetics of halogenated organic compound degradation by iron metal. Environ Sci Technol 30:2634–2640.

Kappler A, Haderlein SB. 2003. Natural organic matter as reductant for chlorinated aliphatic pollutants. Environ Sci Technol 37:2714–2719.

Karickhoff SW. 1984. Organic pollutant sorption in aquatic systems. J Hydraul Eng 10:707–735.

Kenneke JF, Weber EJ. 2000. Reductive dehalogenation of halomethanes in natural and model systems: QSAR analysis. In Proceedings, 220th ACS National Meeting, Division of Environmental Chemistry, Washington, DC, USA, August 20-25, pp 313–315.

Kenneke JF, Weber EJ. 2003. Reductive dehalogenation of halomethanes in iron- and sulfate-reducing sediments. 1. Reactivity pattern analysis. Environ Sci Technol 37:713–720.

Kohn T, Livi KJT, Roberts AL, Vikesland PJ. 2005. Longevity of granular iron in groundwater treatment processes: Corrosion product development. Environ Sci Technol 39:2867–2879.

Kriegman-King MR, Reinhard M. 1991. Reduction of hexachloroethane and carbon tetrachloride at surfaces of biotite, vermiculite, pyrite, and marcasite. In Baker R, ed, Organic Substances and Sediments in Water, Vol 2. Lewis, MI, USA, pp 349–364.

Kriegman-King MR, Reinhard M. 1992. Transformation of carbon tetrachloride in the presence of sulfide, biotite, and vermiculite. Environ Sci Technol 26:2198–2206.

Kriegman-King MR, Reinhard M. 1994. Transformation of carbon tetrachloride by pyrite in aqueous solution. Environ Sci Technol 28:692–700.

Krone UE, Thauer RK, Hogenkamp HPC. 1989. Reductive dehalogenation of chlorinated C1-hydrocarbons mediated by corrinoids. Biochemistry 28:4908–4914.

Krone UE, Thauer RK, Hogenkamp HPC, Steinbach K. 1991. Reductive formation of carbon monooxide from CCl_4 and FREON's 11, 12, 13 catalyzed by corrinoids. Biochemistry 30:2713–2719.

Lee W, Batchelor B. 2002a. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 1. Pyrite and Magnetite. Environ Sci Technol 36:5147–5154.

Lee W, Batchelor B. 2002b. Abiotic reductive dechlorination of chlorinated ethylenes by iron bearing soil minerals. 2. Green rust. Environ Sci Technol 36:5348–5354.

Li T, Farrell J. 2001. Electrochemical investigation of the rate-limiting mechanisms for trichloroethylene and carbon tetrachloride reduction at iron surfaces. Environ Sci Technol 35:3560–3565.

Li T, Farrell J. 2002. Mechanisms controlling chlorocarbon reduction at iron surfaces. In Lipnick RL, Mason RP, Phillips ML, Pittman CU, eds, Chemicals in the Environment: Fate Impacts, and Remediation. ACS, Washington, DC, USA, pp 397–410.

Lien H-L, Zhang W. 2005. Hydrodechlorination of chlorinated ethanes by nanoscale Pd/Fe bimetallic particles. J Environ Eng 131:4–10.

Liu Z, Betterton EA, Arnold RG. 2000. Electrolytic reduction of low molecular weight chlorinated aliphatic compounds: Structural and thermodynamic effects on process kinetics. Environ Sci Technol 34:804–811.

Lovley DR. 1991. Dissimilatory Fe(III) and Mn(IV) reduction. Microbiol Rev 55:259–287.

Lovley DR, Coates JD, Blunt-Harris EL, Phillips EJP, Woodward JC. 1996. Humic substances as electron acceptors for microbial respiration. Nat 382:445–448.

Ma H, O'Loughlin EJ, Burris DR. 2001. Factors affecting humic-nickel complex mediated reduction of trichloroethene in homogeneous aqueous solution. Environ Sci Technol 35:717–724.

Macalady DL, Ranville JF. 1998. The chemistry and geochemistry of natural organic matter. In Macalady DL, ed, Perspectives in Environmental Chemistry. Oxford University Press, New York, NY, USA, pp 94–137.

Mackay DM, Ball WP, Durant MG. 1986a. Variability of aquifer sorption properties in a field experiment on groundwater transport of organic solutes: Methods and preliminary results. J Contam Hydrol 1:119–132.

Mackay DM, Freyberg DL, Roberts PV. 1986b. A natural gradient experiment on solute transport in a sand aquifer. 1. Approach and overview of plume movement. Water Resour Res 22:2017–2029.

Mackay D, Shiu WY, Ma KC. 1993. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Lewis Publishers, Chelsea, MI, USA.

Mader BT, Goss KU, Eisenreich SJ. 1997. Sorption of nonionic, hydrophobic organic chemicals to mineral surfaces. Environ Sci Technol 31:1079–1086.

Maithreepala RA, Doong R-A. 2004. Reductive dechlorination of carbon tetrachloride in aqueous solutions containing ferrous and copper ions. Environ Sci Technol 38:6676–6684.

Matheson LJ, Tratnyek PG. 1994. Reductive dehalogenation of chlorinated methanes by iron metal. Environ Sci Technol 28:2045–2053.

McCormick ML, Adriaens P. 2004. Carbon tetrachloride transformation on the surface of nanoscale biogenic magnetite particles. Environ Sci Technol 38:104–1053.

McCormick ML, Bouwer EJ, Adriaens P. 2002. Carbon tetrachloride transformation in a model iron-reducing culture: Relative kinetics of biotic and abiotic reactions. Environ Sci Technol 36:403–410.

Mendoza CA, Frind EO. 1990a. Advective-dispersive transport of dense organic vapors in the unsaturated zone. 2. Sensitivity analysis. Water Resour Res 26:388–398.

Mendoza CA, Frind EO. 1990b. Advective-dispersive transport of dense organic vapors in the unsaturated zone. 1. Model development. Water Resour Res 26:379–387.

Miehr R, Tratnyek PG, Bandstra JZ, Scherer MM, Alowitz M, Bylaska EJ. 2004. The diversity of contaminant reduction reactions by zero-valent iron: Role of the reductate. Environ Sci Technol 38:139–147.

Miller PL, Vasudevan D, Gschwend PM, Roberts AL. 1998. Transformation of hexachloroethane in a sulfidic natural water. Environ Sci Technol 32:1269–1275.

Moelwyn-Hughes EA. 1949. The kinetics of certain reactions between methyl halides and anions in water. In Proceedings of the Royal Society of London Series A, Mathematical and Physical Sciences 196:540–553.

Nealson KH, Myers CR. 1992. Microbial reduction of manganese and iron: New approaches to carbon cycling. App Environ Microbiol 58:439–443.

Nguyen TH, Goss K, Ball WP. 2005. Polyparameter linear free energy relationships for estimating the equilibrium partition of organic compounds between water and the natural organic matter in soils and sediments. Environ Sci Technol 39:913–924.

Novak PJ, Daniels L, Parkin GF. 1998. Rapid dechlorination of carbon tetrachloride and chloroform by extracellular agents in cultures of methanosarcina thermophila. Environ Sci Technol 32:3132–3136.

Nurmi JT, Tratnyek PG, Sarathy V, Baer DR, Amonette JE, Pecher K, Wang C, Linehan JC, Matson DW, Penn RL, Driessen M. 2005. Characterization and properties of metallic iron nanoparticles: Spectroscopy, electrochemistry and kinetics. Environ Sci Technol 39:1221–1230.

O'Loughlin EJ, Burris DR. 2004. Reduction of halogenated ethanes by green rust. Environ Toxicol Chem 23:41–48.

O'Loughlin EJ, Burris DR, Delcomyn CA. 1999. Reductive dechlorination of trichloroethene mediated by humic-metal complexes. Environ Sci Technol 33:1145–1147.

O'Loughlin EJ, Kemner KM, Burris DR. 2003. Effects of Ag(I), Au(III), and Cu(II) on the reductive dechlorination of carbon tetrachloride by green rust. Environ Sci Technol 37:2905–2912.

Oh S-Y, Cha DK, Chiu PC. 2002. Graphite-mediated reduction of 2,4-dinitrotoluene with elemental iron. Environ Sci Technol 36:2178–2184.

Pankow JF, Cherry JA. 1996. Dense Chlorinated Solvents and Other DNAPLs in Groundwater: History, Behavior, and Remediation. Waterloo Press, Portland, OR, USA.

Pankow JF, Feenstra S, Cherry JA, Ryan MC. 1994. Dense Chlorinated Solvents in Groundwater: A History of the Problem. In Pankow JF, ed, Dense Chlorinated Solvents in Groundwater Systems: Principles Affecting Fate, Transport, and Remediation. Waterloo Press, Portland, OR, USA. 525 p.

Pecher K, Haderlein SB, Schwarzenbach RP. 2002. Reduction of polyhalogenated methanes by surface-bound Fe(II) in aqueous suspensions of iron oxides. Environ Sci Technol 36:1734–1741.

Pedersen HD, Postma D, Jakobsen R, Larsen O. 2005. Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). Geochim Cosmochim Acta 69:3967–3977.

Perlinger JA, Eisenreich SJ, Capel PD. 1993. Application of headspace analysis to the study of sorption of hydrophobic organic chemicals to alpha-Al_2O_3. Environ Sci Technol 27:928–937.

Perlinger JA, Angst W, Schwarzenbach RP. 1996. Kinetics of the reduction of hexachloroethane by juglone in solutions containing hydrogen sulfide. Environ Sci Technol 30:3408–3417.

Perlinger JA, Buschmann J, Angst W, Schwarzenbach RP. 1998. Iron porphyrin and mercaptojuglone mediated reduction of polyhalogenated methanes and ethanes in homogeneous aqueous solution. Environ Sci Technol 32:2431–2437.

Perlinger JA, Venkatapathy R, Harrison JF. 2000. Linear free energy relationships for polyhalogenated alkane transformation by electron transfer mediators in model aqueous systems. J Phys Chem A 104:2752–2763.

Perlinger JA, Kalluri VM, Venkatapathy R, Angst W. 2002. Addition of hydrogen sulfide to juglone. Environ Sci Technol 36:2663–2669.

Pignatello JJ, Xing B. 1996. Mechanisms of slow sorption to organic chemicals to natural particles. Environ Sci Technol 30:1–11.

Rickard DT. 1969. The chemistry of iron sulphide formation at low temperatures. Stockholm Contributions Geol 26:67–95.

Roberts AL, Gschwend PM. 1991. Mechanism of pentachloroethane dechlorination to tetrachloroethylene. Environ Sci Technol 25:76–86.

Roberts AL, Totten LA, Arnold WA, Burris DR, Campbell TJ. 1996. Reductive elimination of chlorinated ethylenes by zero-valent metals. Environ Sci Technol 30:2654–2659.

Roberts PV, Goltz NM, Mackay DM. 1986. A natural gradient experiment on solute transport in a sand aquifer. 3. Retardation estimates and mass balances for organic solutes. Water Resour Res 22:2046–2058.

Rügge K, Hofstetter TB, Haderlein SB, Bjerg PL, Knudsen S, Zraunig C, Mosbæk H, Christensen TH. 1998. Characterization of predominant reductants in an anaerobic leachate-contaminated aquifer by nitroaromatic probe compounds. Environ Sci Technol 32:23–31.

Sawyer CN, McCarty PL, Parkin GF. 1994. Chemistry for Environmental Engineering. McGraw-Hill, Inc., New York, NY, USA.

Schanke CA, Wackett LP. 1992. Environmental reductive elimination reactions of polychlorinated ethanes mimicked by transition-metal coenzymes. Environ Sci Technol 26:830–833.

Scherer MM, Balko BA, Gallagher DA, Tratnyek PG. 1998a. Correlation analysis of rate constants for dechlorination by zero-valent iron. Environ Sci Technol 32:3026–3033.

Scherer MM, Balko BA, Tratnyek PG. 1998b. The role of oxides in reduction reactions at the metal-water interface. In Sparks D, Grundl T, eds, Mineral-Water Interfacial Reactions: Kinetics and Mechanisms, ACS Symposium Series No. 715. ACS, Washington, DC, USA, pp 301–322.

Schwarzenbach RP, Westall J. 1981. Transport of nonpolar organic compounds from surface water to groundwater: Laboratory sorption studies. Environ Sci Technol 15:1360–1367.

Schwarzenbach RP, Stierli R, Lanz K, Zeyer J. 1990. Quinone and iron porphyrin mediated reduction of nitroaromatic compounds in homogeneous aqueous solution. Environ Sci Technol 24:1566–1574.

Schwarzenbach RP, Gschwend PM, Imboden DM. 2003. Environmental Organic Chemistry. John Wiley & Sons, Inc., Hoboken, NJ, USA.

Schwille F. 1984. Migration of organic fluids immiscible with water. In Yaron B, Dagan G, Goldshmid J, eds, Pollutants in Porous Media. Springer-Verlag, New York, NY, USA, pp 27–48.

Schwille F. 1988. Dense Chlorinated Solvents in Porous and Fractured Media-Model Experiments. Boca Raton, FL, USA.

Smolen JM, McLaughlin MA, McNevin MJ, Haberle A, Swantek S. 2003. Reductive dissolution of goethite and the subsequent transformation of 4-cyanonitrobenzene: Role of ascorbic acid and pH. Aquatic Sci 65:1–8.

Song H, Carraway ER. 2005. Reduction of chlorinated ethanes by nanosized zero-valent iron: Kinetics, pathways and effects of reaction conditions. Environ Sci Technol 39:6237–6245.

Stone AT, Godtfredsen KL, Deng B. 1994. Sources and reactivity of reductants encountered in aquatic environments. In Bidoglio G, Stumm W, eds, Chemistry of Aquatic Systems: Local and Global Perspectives. Kluwer Academic, Boston, MA, USA, pp 337–374.

Stumm W. 1992. Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface of Natural Systems. Wiley, New York, NY, USA.

Stumm W, Morgan J. 1996. Aquatic Chemistry. John Wiley & Sons, New York, NY, USA.

Támara ML, Butler EB. 2004. Effects of iron purity and groundwater characteristics on rates and products in the degradation of carbon tetrachloride by iron metal. Environ Sci Technol 38:1866–1876.

Thomas RG. 1982a. Volatilization from Water. In Lyman WJ, Reehl WF, Rosenblatt DH, eds, Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds. McGraw-Hill, New York, NY, USA, pp 15.1–15.34.

Thomas RG. 1982b. Volatilization from Soil. In Lyman WJ, Reehl WF, Rosenblatt DH, eds, Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds. McGraw-Hill, New York, NY, USA, pp 16.1–16.50.

Totten LA, Roberts AL. 2001. Calculated one- and two-electron reduction potentials and related molecular descriptors for reduction of alkyl and vinyl halides in water. Crit Rev Environ Eng Sci Technol 31:175–221.

Tratnyek PG, Macalady DL. 1989. Abiotic reduction of nitro aromatic pesticides in anaerobic laboratory systems. J Agric Food Chem 37:248–254.

Tratnyek PG, Weber EJ, Schwarzenbach RP. 2003. Quantitative structure-activity relationships for chemical reduction of organic contaminants. Environ Toxicol Chem 22:1733–1742.

Vollhardt KPC, Schore NE. 1994. Organic Chemistry. WH Freeman and Company, New York, NY, USA.

Walraevens R, Trouillet P, Devos A. 1974. Basic elimination of HCl from chlorinated ethanes. Int J Chem Kinet 6:777–786.

Weber Jr WJ, DiGiano FA. 1996. Process Dynamics in Environmental Systems. Wiley-Interscience, New York, NY, USA.

Weber Jr WJ, McGinley PM, Katz LE. 1992. A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments. Environ Sci Technol 26:1955–1962.

Williams AGB, Scherer MM. 2004. Spectroscopic evidence for Fe(II)-Fe(III) electron transfer at the Fe oxide-water interface. Environ Sci Technol 38:4782–4790.

Xing B, Pignatello JJ. 1997. Dual-mode sorption of low-polarity compounds in glassy poly (vinylchloride) and soil organic matter. Environ Sci Technol 31:792–799.

Zachara JM, Kukkadapu RK, Fredrickson JK, Gorby YA, Smith SC. 2002. Biomineralization of poorly crystalline Fe(III) oxides by dissimilatory metal reducing bacteria (DMRB). Geomicrobiol J 19:179–207.